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TITLE: OPTICAL INFORMATION RECORDING MEDIUM AND METHOD FOR

OPTICAL INFORMATION RECORDING AND REPRODUCING

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ABSTRACT:

PROBLEM TO BE SOLVED: To provide an optical information recording medium in which information can be recorded with laser light in the recording and reproducing wavelength region for a DVD-R and in 390 to 440 nm wavelength region and to provide a method for optical information recording and reproducing to record information in the medium at the above short wavelength and to reproduce the information recorded in the medium by using a conventional recording and reproducing system for a DVD-R.

SOLUTION: The optical information recording medium has a recording layer containing a dye compound in which information can be recorded by irradiation of laser light on a board. The recording layer is formed in such a

manner that

it shows $\geq 20\%$ reflectance for laser light in the wavelength region from 390

to 440 nm and for laser light in the wavelength region from 620 to 690 nm and

that the real part n and the absolute value k of the imaginary part of the

complex refractive index satisfy $n \geq 1.8$ and $0.02 < k < 0.5$, respectively.

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(54) 【発明の名称】 光情報記録媒体及び光情報記録再生方法

(57) 【要約】

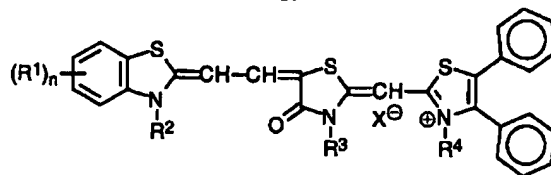
【課題】 DVD-R用の記録再生波長域と390～440nmの範囲の波長域のレーザ光によって情報の記録が可能な光情報記録媒体、及びこの媒体を利用して上記短波長で記録した情報を既存のDVD-R用の記録再生システムを利用して再生する光情報記録再生方法を提供すること。

【解決手段】 基板上にレーザ光の照射による情報の記録が可能な色素化合物を含む記録層を有する光情報記録媒体であって、記録層が、390～440nmの範囲の波長域のレーザ光及び620～690nmの範囲の波長域のレーザ光に対する反射率が20%以上で、その複素屈折率の実数部 n 、及びその虚数部の絶対値 k が、それぞれ $n \geq 1.8$ 、 $0.02 < k < 0.5$ の関係を満たすように形成されていることを特徴とする光情報記録媒体。

【特許請求の範囲】

【請求項1】 基板上にレーザ光の照射による情報の記録が可能な色素化合物を含む記録層を有する光情報記録媒体であって、該記録層が、390～440 nmの範囲の波長のレーザ光及び620～690 nmの範囲の波長のレーザ光のそれぞれに対する反射率が20%以上であって、該記録層の複素屈折率の実数部 n およびその虚数部の絶対値 k が、 $n \geq 1.8$ で、かつ $0.02 < k < 0.5$ の関係を満たすように形成されていることを特徴とする光情報記録媒体。

* 10



【上記の一般式において、 R^1 、 R^2 、 R^3 、そして R^4 は、互いに独立に、炭素数が1～6の飽和もしくは不飽和のアルキル基であり、 n は1～4の整数であり、そして X^- は有機もしくは無機対イオンである。】

【請求項4】 請求項1乃至3のうちの何れかの項に記載の光情報記録媒体に、390～440 nmの範囲の波長のレーザ光を照射して情報を記録した後、620～690 nmの範囲の波長のレーザ光を照射して情報を再生することを特徴とする光情報記録再生方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、レーザ光の照射により情報の記録と読み取りとが可能な光情報記録媒体に関する。更に詳しくは、本発明は、二つの波長域においてレーザ光の照射によって情報の記録と読み取りとが可能な光情報記録媒体及び光情報記録再生方法に関する。

【0002】

【従来の技術】レーザ光の照射によって一回限りの情報の記録が可能な追記型光情報記録媒体（所謂CD-R型の光ディスク）が実用化されている。CD-R型の光ディスクは、一般に円盤状基板上に色素からなる記録層、そして金属からなる反射層をこの順に設け、更に樹脂からなる保護層が塗布により反射層上にこれを覆うように設けられた構造を有している。

【0003】CD-R型の光ディスクより短波長のレーザ光を用いて記録再生を行うことができる光ディスクとして、追記型DVD（デジタル・ビデオ・ディスク：DVD-R）が提案されている（例えば、「日経ニューメディア」別冊「DVD」、1995年発行）。DVD-R型の光ディスクとしては、照射されるレーザ光のトラッキングのための案内溝（アングラー）がCD-R型の光ディスクに比べて半分以上と狭く形成された透明な円盤状基板上に、有機色素からなる記録層、そして通常は記録層の上に更に反射層および保護層を設けてなる二枚※50

*【請求項2】 色素化合物が、その吸収曲線において少なくとも主吸収と副吸収の二つ以上の吸収極大波長を有するものであり、その副吸収の長波長側の端部が、390～440 nmの範囲の波長域にある請求項1に記載の光情報記録媒体。

【請求項3】 色素化合物が、下記の一般式で示されるローダシアニン化合物である請求項1又は2に記載の光情報記録媒体。

【化1】

※の積層体を、それぞれの該記録層を内側にして接着剤で貼り合わせた構造のもの、あるいは上記二枚で構成される積層体のうち、その一枚を円盤状保護板に代えて、一方の基板のみに記録層、反射層及び保護層を順に設けた構成のものが一般的である。このタイプの光ディスクは、CD-R型の光ディスクに比べて6～8倍容量の記録が可能であるとされている。

【0004】上記CD-RやDVD-Rへの情報の書き込み（記録）及び読み取り（再生）は、可視レーザ光（通常CD-Rは、750～800 nm、DVD-Rは、600～700 nmの波長の範囲のレーザ光）を照射することにより行なわれる。即ち、上記のレーザ光を光ディスクに照射すると、色素記録層の照射部分はその光を吸収して局所的に温度上昇し、物理的あるいは化学的に変化（例えば、ビットなどの生成）し、その光学的特性が変化することにより情報の記録が行われる。一方、情報の読み取りも通常は、記録用のレーザ光と同じ波長のレーザ光を光ディスクに照射することにより行われ、色素記録層の光学的特性が変化した部位（ビットなどの生成による記録部分）と変化しない部位（未記録部分）との反射率の違いを検出することにより実施される。

【0005】最近、インターネット等のネットワークやハイビジョンTVの急速な普及に伴って、画像情報を安価簡便に記録するための大容量の記録媒体の要求が高まっている。このような要求に対して、DVD-Rよりも更に短波長のレーザ光を用いることによって記録密度を向上させ、より大きな記録容量を備えた光ディスクの開発が進められている。例えば特開平11-53758号公報には、有機色素を含む記録層、及び銀又はその合金から形成された光反射層が設けられた構成の光情報記録媒体において、記録層側から光反射層側に向けて波長530 nm以下のレーザ光を照射することによって、情報の記録再生を行う記録再生方法が開示されている。具体

的には、記録層の色素として、金属アゾ系色素、キノフタロン系色素またはトリメチンシアニン色素を用いた光ディスクに、青色（波長410nm）又は青緑色（波長515nm）の半導体レーザ光を照射することにより情報の記録再生を行う情報記録再生方法が提案されている。

【0006】また、特開昭58-56239号公報には、複数の色素を混合した記録層であって、400～900nmの全ての波長で80%以上の光吸収率を有して、レーザ光源の変更にも対応できるようにされた光記録媒体が記載されている。特開平10-181211号公報には、620～690nmで記録再生が可能で、 n が1.6～4.0、 k が0.01～0.45、最大吸収ピーク波長が500～655nmのシアニン色素含有記録層を有するDVD-R用光記録媒体が記載されている。

【0007】特許公報（登録）第2925121号には、吸収極大が600～900nmの二種以上のシアニン色素、そして吸収極大が350～600nmのアゾ色素を含有する記録層を持つ、耐光性が向上した光情報記録媒体が記載されている。特開平10-162429号公報には、770～830nmの波長範囲に情報の記録と再生が可能であって、かつ630～680nmでの情報の再生が可能なCD-RあるいはDVD-Rなどの光情報記録媒体が記載されている。特開平9-66671号公報には、780nm及び630～650nmでの n と k とをそれぞれ特定した記録層で、オレンジブック規格に対応し、短波長での記録再生が可能とされた光情報記録媒体が記載されている。

【0008】

【発明が解決しようとする課題】上記特開平11-53758号公報に記載のように記録波長を更に短波長化することにより、より大きな記録容量の光情報記録媒体の設計が可能になる。そして記録した画像情報は、通常短波長専用の記録再生システムを用いて記録用のレーザ光とはほぼ同じ波長域のレーザ光を用いて再生するが、上記のように短波長で記録した画像情報をDVD-R用として利用されている既存の記録再生システムを用いて再生することができれば、便利である。

【0009】本発明の課題は、DVD-R用の記録再生波長領域とこれより更に短波長の波長域のレーザ光、特に390～440nmの範囲の波長のレーザ光によって情報の記録が可能な光情報記録媒体を提供することである。また、本発明の課題は、上記のような短波長で記録した情報を既存の記録再生システムを利用して再生することができる光情報記録媒体及び光情報記録再生方法を提供することでもある。

【0010】

【課題を解決するための手段】本発明者の研究により、光情報記録媒体の記録層の光学定数を特定の範囲となる

ように設定することで、DVD-R用のレーザ光及び青色あるいは青紫色のレーザ光に対して良好な記録再生特性を示す光情報記録媒体を製造できることが見出された。具体的には、上記のような二つのレーザ光の波長域に対してそれらの波長域よりもそれぞれ短波長側に吸収極大波長を有するような吸収曲線を有する特定のローダシアニン化合物を記録材料として用いることにより、目的とする光情報記録媒体を製造できることが見出された。

10 【0011】本発明は、基板上にレーザ光の照射による情報の記録が可能な色素化合物を含む記録層を有する光情報記録媒体であって、該記録層が、390～440nmの範囲の波長のレーザ光及び620～690nmの範囲の波長のレーザ光のそれぞれに対する反射率が20%以上（好ましくは30%以上、さらに好ましくは40%以上）であって、該記録層の複素屈折率の実数部 n およびその虚数部の絶対値 k が、 $n \geq 1.8$ で、かつ $0.02 < k < 0.5$ の関係を満たすように形成されていることを特徴とする光情報記録媒体にある。

20 【0012】また、本発明は、上記のような構成の光情報記録媒体に、390～440nmの範囲の波長のレーザ光を照射して情報を記録した後、620～690nmの範囲の波長のレーザ光を照射して情報を再生することを特徴とする光情報記録再生方法にもある。

【0013】本発明の光情報記録媒体及び光情報記録再生方法は以下の態様であることが好ましい。

（1）390～440nmの範囲の波長のレーザ光及び620～690nmの範囲の波長のレーザ光に対する記録層の複素屈折率の実数部 n が、 $n \geq 2.0$ （更に好ましくは、 $n \geq 2.1$ 、特に好ましくは、 $n \geq 2.2$ ）である。

（2）記録層が、620～690nmの範囲の波長のレーザ光に対して、 $0.05 \leq k \leq 0.3$ （更に好ましくは、 $0.08 \leq k \leq 0.25$ 、特に好ましくは、 $0.1 \leq k \leq 0.2$ ）の関係を満たすように形成されている光情報記録媒体。

【0014】（3）記録層が、390～440nmの範囲の波長のレーザ光に対して、 $0.03 \leq k \leq 0.3$

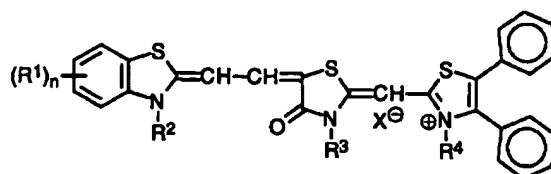
（更に好ましくは、 $0.04 \leq k \leq 0.25$ 、特に好ましくは、 $0.05 \leq k \leq 0.2$ ）の関係を満たすように形成されている光情報記録媒体。

（4）色素化合物が、その吸収曲線において少なくとも二つ以上の吸収極大波長を有するものであり、その副吸収の長波長側の端部が、390～440nmの範囲のレーザ光の波長域にある光情報記録媒体。

（5）色素化合物が、下記の一般式で示されるローダシアニン化合物である光情報記録媒体：

【0015】

【化2】



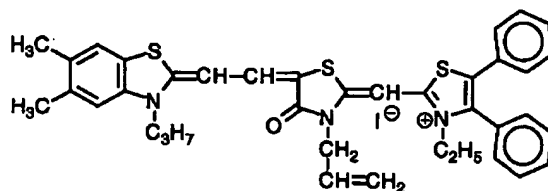
【0016】[上記の一般式において、 R^1 、 R^2 、 R^3 、そして R^4 は、互いに独立に、炭素数が1～6の飽和もしくは不飽和のアルキル基であり、 n は1～4の整数であり、そして X^- は有機もしくは無機の対イオンである]。

*【0017】(6) 色素化合物が、下記式で示されるローダシアニン化合物である光情報記録媒体：

【0018】

【化3】

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【0019】(7) 記録層の厚みが、プレグループ内において、50～200 nm (好ましくは、60～150 nm、特に好ましくは、65～120 nm) の範囲にある。

【0020】

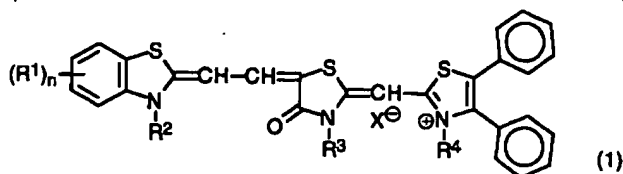
【発明の実施の形態】本発明の光情報記録媒体(光ディスクと称する場合がある)は、透明な円盤状基板上にレーザー光の照射により情報を記録することができる色素化合物を含む記録層を有する。そして記録層が、390～440 nmの範囲の波長のレーザー光及び620～690 nmの範囲の波長のレーザー光に対する反射率が共に20%以上であって、かつ記録層の複素屈折率の実数部 n 、及びその虚数部の絶対値 k が、それぞれ $n \geq 1.8$ で、かつ $0.02 < k < 0.5$ の関係を満たすように形成されていることを特徴とするものである。具体的には、記録層の光学特性が上記のような関係を満たすように、色素化合物を選定して用いる。

【0021】一般に複素屈折率 n_0 は、 $n_0 = n - ik$ (n : 屈折率、 k : 消衰係数)の式で与えられる。そして色素化合物を含む記録層の複素屈折率は、用いるレーザー光の波長によって変化する。本発明の光情報記録媒体では、620～690 nm (好ましくは、630～660 nm) の波長のレーザー光及び390～440 nmの範囲の波長のレーザー光が使用されるために、この二つの波長域のレーザー光に対して記録層が上記の関係式を満たすように調整されている。そして、本発明の光情報記録媒体が、より良好な感度を得られ、優れた記録特性を示すためには、620～690 nmの範囲の波長のレーザー光に対して、 k は、 $0.02 \leq k \leq 0.3$ (更に好ましくは、 $0.04 \leq k \leq 0.25$ 、特に好ましくは、 $0.0 \leq k \leq 0.2$) の範囲にあることが好ましい。また、390～440 nmの範囲の波長のレーザー光に対しては、 k は、 $0.03 \leq k \leq 0.3$ (更に好ましくは、 $0.04 \leq k \leq 0.25$ 、特に好ましくは、 $0.05 \leq k \leq 0.2$) の範囲にあることが好ましい。一方、再生特性においては、より大きな変調度を与えるために、上記の二つのレーザー光の波長域に対して、 n は、 $n \geq 2.0$ (更に好ましくは、 $n \geq 2.2$ 、特に好ましくは $n \geq 2.5$) の関係を満たしていることが好ましい。

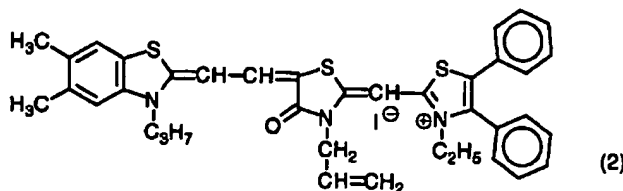
【0022】記録層に使用する色素化合物は、記録層の光学特性が上記のような関係を満たすものであれば特に限定されないが、390～440 nmの範囲のレーザー光の波長域に対して、その吸収曲線の副吸収を利用できるものであることが好ましい。例えば、本発明に用いる色素化合物は、その吸収曲線において、少なくとも二つ以上の吸収極大波長を有するものであり、その副吸収の長波長側の端部が、390～440 nmの範囲のレーザー光の波長域にあるものであることが好ましい。即ち、色素化合物が、短波長側のレーザー光の波長域よりも更に短波長側にその副吸収の極大波長を有する(色素化合物の副吸収の極大波長は、短波長側のレーザー光の波長域よりも更に短波長側にずれている、一般に、このずれは、 ± 20 nmの範囲にある)ものであることが好ましい。このような吸収曲線を持つ好ましい色素化合物としては、例えば、下記一般式(1) [式中の記号の意味は前記の通りである]、特に下記式(2)で示されるローダシアニン化合物を挙げることができる。

【0023】

【化4】



(1)



(2)

【0024】図1は、上記色素化合物の青色あるいは青紫色～赤色の波長域における吸収スペクトル（吸収曲線）を示すものである。例えば、後述するように本発明の実施例で用いた408nm（青紫色）の波長のレーザー光に対しては、上記色素化合物の約390nmの副吸収極大（副吸収ピーク）を利用することにより、記録再生を行うことができる。一方、638nm（赤色）の波長のレーザー光に対しては、その色素化合物の600nmの主吸収極大（主吸収ピーク）を利用して同様に記録再生を行うことができる。

【0025】次に、上記のような光学特性を有する記録層を基板上に設けた本発明の光情報記録媒体の製造法を説明する。本発明の光情報記録媒体は、基板上に記録層を設けることにより製造される。本発明の光情報記録媒体は種々の構成を採ることができる。採りうる構成としては、例えば、透明な円盤状基板上に記録層及び反射層をこの順に有する構成、該円盤状基板上に記録層、反射層及び保護層をこの順に有する構成、あるいは該円盤状基板上に記録層及び反射層、更に所望により保護層が設けられた積層体二枚を、それぞれ記録層側が内側となるように接着剤層により接合した構成のもの、あるいは該積層体と円盤状保護基板（該基板には、記録層以外の反射層などが設けられていてもよい）とを記録層側が内側となるように同様に接合した構成のものなどを挙げることができる。これらの構成の場合には、透明な基板側からレーザー光を照射する。

【0026】又、光情報記録媒体を、円盤状基板上に反射層、記録層及び保護層を順に有する構成、円盤状基板、接着剤層、円盤状基板、反射層、記録層及び保護層を順に有する構成、あるいは保護層、記録層、反射層、円盤状基板、接着剤層、円盤状基板、反射層、記録層及び保護層を順に有する構成を採ることも可能である。これらの構成の場合には、レーザー光を保護層側から照射する。尚、これらの構成の場合には、円盤状基板は透明である必要はない。本発明の光情報記録媒体は、前記基板側からレーザー光を照射する態様であることが好ましい。以下に、透明な円盤状基板上に記録層のみを有する構成の光情報記録媒体を例にとって本発明の光情報記録媒体* 50

*の製造法を詳述する。

【0027】基板は、従来の光情報記録媒体の基板として用いられている各種の材料から任意に選択することができる。基板材料としては、例えば、ガラス；ポリカーボネート；ポリメチルメタクリレート等のアクリル樹脂；ポリ塩化ビニル、塩化ビニル共重合体等の塩化ビニル系樹脂；エポキシ樹脂；アモルファスポリオレフィンおよびポリエステル等を挙げることができ、所望によりそれらを併用してもよい。なお、これらの材料はフィルム状としてまたは剛性のある基板として使うことができる。上記材料の中では、耐湿性、寸法安定性および価格などの点からポリカーボネートが好ましい。

【0028】上記基板の記録層が設けられる側の表面には、一定のトラックピッチのプレグループが形成されていることが好ましい。本発明の光情報記録媒体の基板上に形成されるプレグループのトラックピッチは、従来のDVD-R用に形成されるトラックピッチに合うように、例えば、0.5～1.0μm（更に好ましくは、0.6～0.9μm）に設定することも可能であるが、390～440nmの範囲のレーザー光（記録光）に合わせて、更に狭く設定することができ、これにより記録密度を増大することができる。このように短波長のレーザー光に合わせたプレグループのトラックピッチは、0.25～0.7μm（更に好ましくは、0.3～0.55μm、特に好ましくは、0.35～0.50μm）の範囲にあることが好ましい。

【0029】プレグループは、その側壁が55～80°（更に好ましくは、60～80°）の範囲の角度で傾斜していることが好ましい。ここで、側壁の傾斜角度とは、プレグループ（凹状の溝）の底面から該溝の深さの10%の位置における溝の側壁上の点と該溝の深さの50%の位置における溝の側壁上の点とを結ぶ直線の延長と、凹状の溝の底面に水平な面とで形成される角度を意味する。このようにプレグループの側壁の傾斜角度を急な角度とすることで、プレグループのトラックピッチが狭くなってもクロストークを抑制でき、またジッタ値の上昇を抑えることが可能になる。なお、このような形状のプレグループは、例えば、基板を射出成型あるいは押

し出し成型する際に、予め所定の傾斜角度の側壁を持つように加工された樹脂成型用のスタンパ（金型）を用いて形成することができる。

【0030】プレグループの溝形状（深さや幅）においても390～440nmの範囲のレーザ光（記録光）に合わせて、DVD-Rに比べて狭く設定することができる。プレグループの深さは30～170nm（更に好ましくは、50～140nm、特に好ましくは、65～130nm）の範囲にあることが好ましく、またプレグループの幅（半値幅）は、65～300nm（更に好ましくは、95～260nm、特に好ましくは、130～230nm）の範囲にあることが好ましい。

【0031】記録層が設けられる側の基板表面には、平面性の改善および接着力の向上および記録層の変質防止などの目的で、下塗層が設けられてもよい。下塗層の材料としては、例えば、ポリメチルメタクリレート、アクリル酸・メタクリル酸共重合体、スチレン・無水マレイン酸共重合体、ポリビニルアルコール、N-メチロールアクリルアミド、スチレン・ビニルトルエン共重合体、クロルスルホン化ポリエチレン、ニトロセルロース、ポリ塩化ビニル、塩素化ポリオレフィン、ポリエステル、ポリイミド、酢酸ビニル・塩化ビニル共重合体、エチレン・酢酸ビニル共重合体、ポリエチレン、ポリプロピレン、ポリカーボネート等の高分子物質；及びシランカップリング剤などの表面改質剤を挙げることができる。下塗層は、上記物質を適当な溶剤に溶解または分散して塗布液を調製したのち、この塗布液をスピンコート、ディップコート、エクストルージョンコートなどの塗布法を利用して基板表面に塗布することにより形成することができる。下塗層の層厚は一般に0.005～20μmの範囲にあり、好ましくは0.01～10μmの範囲である。

【0032】プレグループの形成は、プレグループ層を設けることにより行っても良い。プレグループ層の材料としては、アクリル酸のモノエステル、ジエステル、トリエステルおよびテトラエステルのうちの少なくとも一種のモノマー（またはオリゴマー）と光重合開始剤との混合物を用いることができる。プレグループ層の形成は、例えば、まず精密に作られた母型（スタンパ）上に上記のアクリル酸エステルおよび重合開始剤からなる混合液を塗布し、更にこの塗布液層上に基板を載せたのち、基板または母型を介して紫外線を照射することにより塗布層を硬化させて基板と塗布層とを固着させる。次いで、基板を母型から剥離することにより得ることができる。プレグループ層の層厚は一般に、0.03～70μmの範囲にあり、好ましくは0.06～35μmの範囲である。

【0033】基板には色素化合物含有記録層が設けられる。記録層の形成は、例えば、前記特定の色素化合物を溶剤に溶解して塗布液を調製し、この塗布液を基板の

前記プレグループが形成されているその表面に塗布して塗膜を形成した後、乾燥することにより、行うことができる。塗布液の調製に際しては、退色防止剤を加えることや、更に所望により結合剤を加えることもできる。

【0034】記録層形成用の塗布液の溶剤の例としては、酢酸ブチル、セロソルブアセテートなどのエステル；メチルエチルケトン、シクロヘキサノン、メチルイソブチルケトンなどのケトン；ジクロルメタン、1,2-ジクロルエタン、クロロホルムなどの塩素化炭化水素；ジメチルホルムアミドなどのアミド；シクロヘキサンなどの炭化水素；テトラヒドロフラン、エチルエーテル、ジオキサンなどのエーテル；エタノール、n-プロパノール、イソプロパノール、n-ブタノール、ジアセトンアルコールなどのアルコール；2,2,3,3-テトラフロロプロパノールなどのフッ素系溶剤；エチレングリコールモノメチルエーテル、エチレングリコールモノエチルエーテル、プロピレングリコールモノメチルエーテルなどのグリコールエーテル類などを挙げることができる。上記溶剤は使用する化合物の溶解性を考慮して単独または二種以上を組み合わせる用いることができる。塗布液中には更に酸化防止剤、UV吸収剤、可塑剤、及び潤滑剤などの各種の添加剤を目的に応じて添加してもよい。

【0035】退色防止剤の代表的な例としては、ニトロソ化合物、金属錯体、ジアンモニウム塩、及びアミニウム塩などを挙げることができる。これらの例は、例えば、特開平2-300288号、同3-224793号、あるいは同4-146189号等の各公報に記載されている。退色防止剤を使用する場合には、その使用量は、色素化合物の量に対して、通常0.1～50重量%の範囲であり、好ましくは、0.5～45重量%の範囲、更に好ましくは、3～40重量%の範囲、特に5～25重量%の範囲である。

【0036】結合剤の例としては、例えばゼラチン、セルロース誘導体、デキストラン、ロジン、ゴムなどの天然有機高分子物質；およびポリウレタン、ポリエチレン、ポリプロピレン、ポリスチレン、ポリイソブチレン等の炭化水素系樹脂；ポリ塩化ビニル、ポリ塩化ビニリデン、ポリ塩化ビニル・ポリ酢酸ビニル共重合体等のビニル系樹脂；ポリアクリル酸メチル、ポリメタクリル酸メチルなどのアクリル樹脂；ポリビニルアルコール、塩素化ポリエチレン、エポキシ樹脂、ブチラール樹脂、ゴム誘導体、フェノール・ホルムアルデヒド樹脂等の熱硬化性樹脂の初期縮合物などの合成有機高分子を挙げることができる。記録層の材料として結合剤を併用する場合に、結合剤の使用量は、色素化合物100重量部に対して0.2～20重量部、好ましくは0.5～10重量部、更に好ましくは1～5重量部である。このようにして調製される塗布液中の色素化合物の濃度は一般に0.01～10重量%の範囲にあり、好ましくは0.1～5

重量%の範囲にある。

【0037】塗布方法としては、スプレー法、スピコート法、ディップ法、ロールコート法、ブレードコート法、ドクターロール法、スクリーン印刷法などを挙げることができる。記録層は単層でも重層でもよい。記録層の層厚（乾燥後の平均厚み）は、一般に10～350nmの範囲にあり、好ましくは、30～250nmの範囲である。本発明の光情報記録媒体の場合、記録層のプレグループ内の厚みは、好ましくは50～200nmの範囲にあり、更に好ましくは、60～150nmの範囲、特に好ましくは、65～120nmの範囲である。又ランド部の厚みは、好ましくは、30～150nmの範囲にあり、更に好ましくは、40～120nmの範囲、特に好ましくは、50～100nmの範囲である。

【0038】以上の工程により、基板上に記録層を有する本発明の光情報記録媒体を製造することができる。

【0039】反射層、及び保護層を設ける場合について以下に説明する。反射層は、一般に情報の再生時における反射率の向上の目的で記録層上、あるいは基板上に設けられる。反射層の材料である光反射性物質はレーザ光に対する反射率が高い物質であり、その例としては、Mg、Se、Y、Ti、Zr、Hf、V、Nb、Ta、Cr、Mo、W、Mn、Re、Fe、Co、Ni、Ru、Rh、Pd、Ir、Pt、Cu、Ag、Au、Zn、Cd、Al、Ga、In、Si、Ge、Te、Pb、Po、Sn、Biなどの金属及び半金属あるいはステンレス鋼を挙げることができる。これらのうちで好ましいものは、Cr、Ni、Pt、Cu、Ag、Au、Alおよびステンレス鋼である。これらの物質は単独で用いてもよいし、あるいは二種以上の組み合わせで、または合金として用いてもよい。特に好ましくは、Au、Ag、及びこれらの金属を含む合金である。反射層は、例えば上記反射性物質を蒸着、スパッタリングまたはイオンプレーティングすることにより記録層上、あるいは基板上に形成することができる。反射層の層厚は一般には5～500nmの範囲にあり、好ましくは10～350nmの範囲、更に好ましくは30～200nmの範囲である。

【0040】保護層は、記録層、及び反射層を物理的及び化学的に保護する目的で設けられる。保護層に用いられる材料としては、例えば、SiO、SiO₂、MgF₂、SnO₂、Si₃N₄などの無機物質、熱可塑性樹脂、熱硬化性樹脂、UV硬化性樹脂等の有機物質を挙げることができる。保護層は樹脂で形成されていることが好ましい。保護層を反射層上に設ける場合、保護層は、例えばプラスチックの押出加工で得られたフィルムを、接着層を介して反射層上にラミネートすることにより形成することができる。あるいは、真空蒸着、スパッタリング、塗布等の方法により保護層を設けてもよい。また、熱可塑性樹脂、熱硬化性樹脂の場合には、これらを適当な溶剤に溶解して塗布液を調製した後、この塗布液

を塗布し、乾燥することによって保護層を形成することができる。UV硬化性樹脂の場合には、そのまましくは適当な溶剤に溶解して塗布液を調製したのちこの塗布液を塗布し、UV光を照射して硬化させることによって保護層を形成することができる。これらの塗布液中には、更に帯電防止剤、酸化防止剤、UV吸収剤等の各種添加剤を目的に応じて添加してもよい。保護層の層厚は一般には0.05～70μmの範囲にある。

【0041】基板上に記録層及び反射層、そして所望により保護層を設けた積層体を二枚用意し、各々の記録層が内側となるように接着剤等で貼り合わせることににより、二つの記録層を有する光情報記録媒体を製造することができる。また得られた積層体と、該積層体の基板と略同じ寸法の円盤状保護基板とを、その記録層が内側となるように接着剤等で貼り合わせることににより、片側のみに記録層を持つ光情報記録媒体を製造することができる。接着は、前記保護層の形成に用いたUV硬化性樹脂や、合成接着剤、あるいはまた両面テープなどを用いて行なうことができる。このようにして形成される接着剤層は、通常は0.05～70μm（好ましくは、3～50μm）の範囲の厚みで設けられる。

【0042】本発明の光情報記録媒体を用いた情報の記録再生方法は、例えば、次のように実施される。光情報記録媒体を所定の定線速度（CDフォーマットの場合は1.2～1.4m/秒の1倍速）または所定の定角速度にて回転させながら、基板側あるいは保護層側から半導体レーザ光などの記録用のレーザ光を光学系を通して集光し、記録層に照射する。レーザ光の照射により、記録層の照射部分はその光を吸収して局所的に温度上昇し、物理的あるいは化学的な変化が生じてその光学特性を変えることにより、情報が記録される。本発明では、記録光として、620～690nmの範囲の赤色光の発振波長を有する半導体レーザービーム、及び390～440nmの範囲の青色光あるいは青紫色光の発振波長を有する半導体レーザービームが用いられる。また記録光は、NAが0.55～0.7の光学系を通して集光されることが好ましい。

【0043】上記のように記録された情報の再生は、記録後の光情報記録媒体を所定の定線速度で回転させながら上記の半導体レーザ光を基板側、あるいは保護層側から照射して、その反射光を検出することにより行われる。本発明の光情報記録媒体は、上記のいずれの範囲の発振波長を持つレーザ光を用いても記録再生することができる。本発明では、青色あるいは青紫色の発振波長を有する半導体レーザービームを用いて記録を行い、赤色の発振波長を有する半導体レーザービームを用いて再生を行う記録再生方法を利用することが好ましい。この方法を利用することで、例えば、記録光として、青色あるいは青紫色レーザー光を用いて画像情報を記録して製作した光情報記録媒体を、記録光と同じ発振波長を持つ専用

の再生システムを用いることなく、DVD-R用として既に汎用されている記録再生システムを利用して再生できる利点がある。

【0044】

【実施例】以下に、本発明の実施例及び比較例を記載する。

【0045】【実施例1】

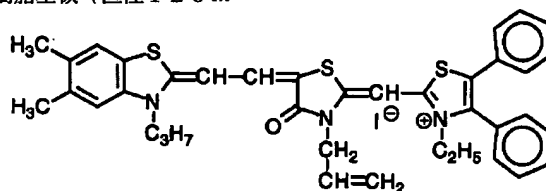
円盤状基板の作製

所定のトラックピッチ及び溝（プレグループ）となるように作製されたスタンプを内蔵する射出成型機を用いてポリカーボネート製（樹脂商品名：パンライトAD5503、帝人（株））の円盤状樹脂基板（直径120mm）*

*m、内径15mm、厚さ0.6mm）を作製した。得られた樹脂基板の凹状の溝（プレグループ）のトラックピッチは、0.48μm、溝の深さは90nm、溝の幅は190nm、そして溝の側壁の傾斜角度（溝の底面から溝の深さの10%の位置における溝の側壁上の点と溝の深さの50%の位置における溝の側壁上の点とを結ぶ直線の延長と、凹状の溝の底面に水平な面とで形成される角度）は60°であった。これらの形状の測定は、AFMを用いて行った。

【0046】

【化5】



【0047】上記色素の溶液中の濃度が1重量%となるように、2, 2, 3, 3-テトラフルオロ-1-プロパノール中に溶解し、記録層形成用塗布液を調製した。この塗布液を、上記で得た円盤状ポリカーボネート基板のそのプレグループが設けられている表面に、スピコート法により塗布し、乾燥して記録層（グループ内の厚さ：120nm、ランド部の厚さ：80nm）を形成し、本発明に従う光情報記録媒体（光ディスク）を製造した。

【0048】【光情報記録媒体としての評価】

（1）得られた光ディスクに下記の記録再生装置を用いて、定線速度3.5m/秒で、周波数1MHzの矩形波の信号を記録パワーを3~10mWまで変化させて最適記録パワーで記録した。

記録再生装置：DDU1000（パルステック社製）

レーザー：408nmの青紫色の発信波長を持つ半導体レーザー

ピックアップNA：0.6

リムインテンシティ：タンジェンシャル方向0.33

ラジアル方向0.21

円偏向ビームを使用し、フォーカスはナイフエッジ法、そしてトラッキングはブッシュブル法を用いて行った。408nmの波長のレーザー光に対して得られた記録層の屈折率nは、2.2であり、消衰係数kは、0.05であった。

【0049】記録後、記録用のレーザー光と同じ波長のレーザー光を用いて0.5mWのレーザーパワーで記録信号を再生し、変調度を測定した。変調度は、上記条件で記録された信号を再生したときの直流再生波形の反射光レベルの極大値をA、極小値をBとして、未記録部でグループトラッキングを行ったときの反射光レベルをRとし ※

※で、下記の式から求めた。

$$\text{変調度}(\%) = (A - B) / R \times 100\%$$

その結果、62%の変調度が得られた。

【0050】（2）上記の記録再生装置に638nmの赤色の発信波長を持つ半導体レーザーを搭載して上記

（1）と同様にして光ディスクに信号を記録した。638nmの波長のレーザー光に対して得られた記録層の屈折率nは、2.3であり、消衰係数kは、0.1であった。その後、同じ波長のレーザー光を用いて再生し、同様な方法で変調度を測定した。その結果、65%の変調度が得られた。

【0051】（3）上記408nmの青紫色の発信波長を持つ半導体レーザーを用いて信号を記録した後、638nmの赤色の発信波長を持つ半導体レーザーを用いて記録した信号を再生したところ、高い解像度で信号を再生することができた。

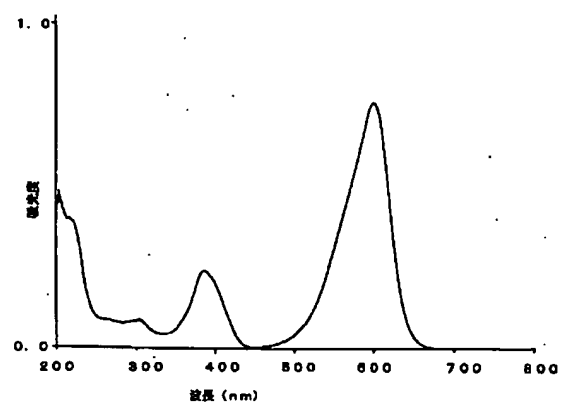
【0052】

【発明の効果】本発明に従う光情報記録媒体を用いることにより、DVD-R用のレーザー光及び青色あるいは青紫色のレーザー光の波長域において記録再生が可能である。しかも本発明に従う光情報記録媒体は、両方の波長域のレーザー光において良好な記録再生特性を示す。従って、青色あるいは青紫色のレーザー光を用いて記録した情報を、DVD-R用のレーザー光を用いて再生することができる。また、青色あるいは青紫色のレーザー光を用いることで、より高密度の記録が可能となり、記録容量の更に大きな光情報記録媒体を製造することができる。

【図面の簡単な説明】

【図1】本発明の光情報記録媒体の記録層に用いられる好ましい色素化合物の吸収スペクトルを示す。

【図1】



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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the optical information record medium [reading / information / record medium / record and reading] by the exposure of a laser beam. Furthermore, this invention relates to the optical information record medium [reading / information / record medium / record and reading], and the optical information record playback approach by the exposure of a laser beam in two wavelength regions in detail.

[0002]

[Description of the Prior Art] The added type light information record medium (the so-called CD-R type of optical disk) of a postscript which can record the information only for 1 time is put in practical use by the exposure of a laser beam. The optical disk of a CD-R mold has the structure which generally prepared the recording layer which consists of coloring matter, and the reflecting layer which consists of a metal on the disc-like substrate at this order, and was established so that the protective layer which consists of resin further might cover this on a reflecting layer by spreading.

[0003] As an optical disk which can perform record playback using the laser beam of short wavelength from the optical disk of a CD-R mold, the postscript mold DVD (digital video disc: DVD-R) is proposed (for example, the "Nikkei new-medium" separate volume "DVD", 1995 issue). As optical De Dis of a DVD-R mold, the guide rail for the tracking of the laser beam irradiated (pre groove) compared with optical ISUKU of a CD-R mold below one half and on the transparent disc-like substrate with which it was formed narrowly The recording layer which consists of organic coloring matter, and the layered product of two sheets which usually comes to prepare a reflecting layer and a protective layer further on a recording layer The thing of a configuration of having replaced with the disc-like guard plate the one the thing of the structure which carries out this each recording layer inside, and was stuck with adhesives, or in the layered product which consists of two above-mentioned sheets, and having prepared the recording layer, the reflecting layer, and the protective layer only in one substrate in order is common. Compared with the optical disk of a CD-R mold, record of capacity of this type of optical disk is enabled six to 8 times.

[0004] Writing (record) and reading (playback) of the information on the above-mentioned CD-R or DVD-R are performed by irradiating visible laser light (CD-R being 750-800nm, and DVD-R being usually the laser beam of the range of 600-700nm wavelength). That is, if the above-mentioned laser beam is irradiated at an optical disk, informational record will be performed, when the exposure part of a coloring matter recording layer absorbs the light, a temperature rise is carried out locally, it changes physically or chemically (for example, generation of a pit etc.) and the optical property changes. On the other hand, reading of information is also performed by usually irradiating the laser beam for record, and the laser beam of the same wavelength at an optical disk, and is carried out by detecting the difference in the reflection factor of the part (record part by generation of a pit etc.) where the optical property of a coloring matter recording layer changed, and the part (non-recorded part) not changing.

[0005] Recently, the demand of the mass record medium for recording image information cheaply

simple is increasing with the rapid spread of networks, such as the Internet, or Hi-Vision TV. To such a demand, by using the laser beam of short wavelength further rather than DVD-R, recording density is raised and development of the optical disk equipped with bigger storage capacity is furthered. For example, in the optical information record medium of a configuration of that the light reflex layer formed in JP,11-53758,A from the recording layer containing organic coloring matter and silver, or its alloy was prepared, the record playback approach of performing informational record playback is indicated by irradiating a laser beam with a wavelength of 530nm or less towards a light reflex layer side from a recording layer side. The information record playback approach of specifically performing informational record playback to the optical disk using metal azo system coloring matter, kino FUTARON system coloring matter, or TORIMECHIN cyanine dye as coloring matter of a recording layer by irradiating the semiconductor laser light of blue (wavelength of 410nm) or a bluish green color (wavelength of 515nm) is proposed.

[0006] Moreover, it is the recording layer which mixed two or more coloring matter, and in JP,58-56239,A, it has 80% or more of rate of light absorption on all the wavelength of 400-900nm, and the optical recording medium which enabled it to correspond also to modification of a laser light source is indicated. To JP,10-181211,A, record playback is possible at 620-690nm, and the optical recording medium for DVD-R with which n has the cyanine dye content recording layer 0.01 to 0.45 and whose maximum absorption peak wavelength 1.6-4.0 μ m are 500-655nm is indicated.

[0007] The optical information record medium which has a recording layer containing two or more sorts of cyanine dye whose absorption maximums are 600-900nm, and the azo dye whose absorption maximum is 350-600nm in the patent official report (registration) No. 2925121 and whose lightfastness improved is indicated. Optical information record media, such as CD-R which can reproduce 630-680nm information, or DVD-R, are indicated possible [informational record and playback] in the wavelength range of 770-830nm by JP,10-162429,A. By the recording layer which specified 630-650nm [780nm and] n and k, respectively, it corresponds to Orange Book specification and the optical information record medium whose record playback with short wavelength was enabled is indicated by JP,9-66671,A.

[0008]

[Problem(s) to be Solved by the Invention] By short-wavelength-izing record wavelength further like a publication to above-mentioned JP,11-53758,A, the design of the optical information record medium of bigger storage capacity is attained. And although it usually reproduces using the laser beam for record, and the laser beam of the almost same wavelength region using the record regeneration system only for short wavelength, the recorded image information is convenient if the image information recorded with short wavelength as mentioned above is reproducible using the existing record regeneration system used as an object for DVD-R.

[0009] The technical problems of this invention are the laser beam of the wavelength region of short wavelength, and offering especially the optical information record medium which can record informational by the laser beam of the wavelength of the range of 390-440nm more nearly further than the record playback wavelength field for DVD-R, and this. Moreover, the technical problem of this invention is also offering the optical information record medium and the optical information record playback approach of doing, although the information recorded with the above short wavelength is reproduced using the existing record regeneration system.

[0010]

[Means for Solving the Problem] It was found out that the optical information record medium in which good record reproducing characteristics are shown by research of this invention person to the laser beam of the laser beam for DVD-R and blue, or a purple-blue color by setting up the optical constant of the recording layer of an optical information record medium so that it may become the specific range can be manufactured. It was found out by using the specific loader cyanine compound which specifically has an absorption curve which has absorption-maximum wavelength in a short wavelength side rather than those wavelength regions to the wavelength region of the two above laser beams, respectively as a record ingredient that the optical information record medium made into the purpose can be

manufactured.

[0011] This invention is an optical information record medium which has on a substrate a recording layer containing the coloring matter compound which can record the information by the exposure of a laser beam. A reflection factor [as opposed to each of the laser beam of the wavelength of the range of 390-440nm and the laser beam of the wavelength of the range of 620-690nm in this recording layer] is 20% or more (30% or more preferably). It is in the optical information record medium which it is 40% or more still more preferably, and the absolute value k of the real part n of the complex index of refraction of this recording layer and its imaginary part is $n \geq 1.8$, and is characterized by being formed so that the relation of $0.02 < k < 0.5$ may be filled.

[0012] Moreover, after this invention irradiates the laser beam of the wavelength of the range of 390-440nm and records information on the above optical information record media of a configuration, it is also in the optical information record playback approach characterized by irradiating the laser beam of the wavelength of the range of 620-690nm, and reproducing information.

[0013] As for the optical information record medium of this invention, and the optical information record playback approach, it is desirable that they are the following modes.

(1) The real part n of the complex index of refraction of a recording layer to the laser beam of the wavelength of the range of 390-440nm and the laser beam of the wavelength of the range of 620-690nm is $n \geq 2.0$ (still more preferably $n \geq 2.1$, especially preferably $n \geq 2.2$).

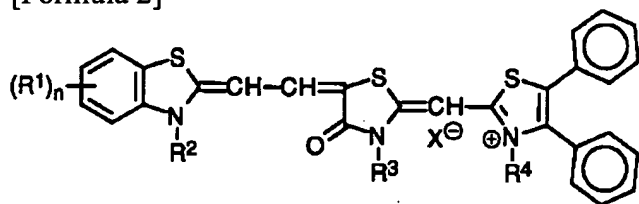
(2) The optical information record medium currently formed so that a recording layer may fill the relation of $0.05 \leq k \leq 0.3$ (still more preferably $0.08 \leq k \leq 0.25$, especially preferably $0.1 \leq k \leq 0.2$) to the laser beam of the wavelength of the range of 620-690nm.

[0014] (3) The optical information record medium currently formed so that a recording layer may fill the relation of $0.03 \leq k \leq 0.3$ (still more preferably $0.04 \leq k \leq 0.25$, especially preferably $0.05 \leq k \leq 0.2$) to the laser beam of the wavelength of the range of 390-440nm.

(4) that in which a coloring matter compound has at least two or more absorption-maximum wavelength in the absorption curve -- it is -- the long wave of the subabsorption -- the optical information record medium which has an edge by the side of merit in the wavelength region of the laser beam of the range of 390-440nm.

(5) Optical information record medium whose coloring matter compound is a loader cyanine compound shown by the following general formula : [0015]

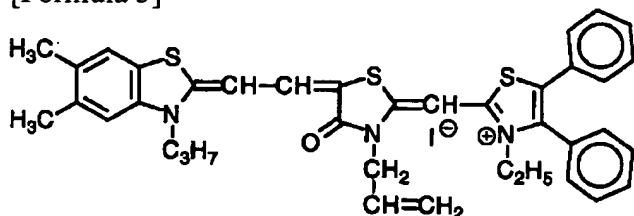
[Formula 2]



[0016] [in the above-mentioned general formula, the carbon number of R_1 , R_2 , R_3 , and R_4 is the alkyl group of the saturation of 1-6, or partial saturation mutually-independent, and n is the integer of 1-4, and X^- is an organic or inorganic counter ion].

[0017] (6) Optical information record medium whose coloring matter compound is a loader cyanine compound shown by the following formula : [0018]

[Formula 3]



[0019] (7) The thickness of a recording layer is in a pre groove in the range of 50-200nm (preferably 60-150nm, especially preferably 65-120nm).

[0020]

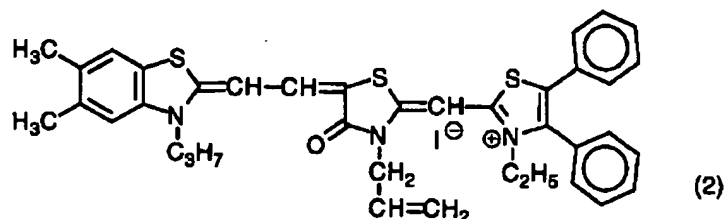
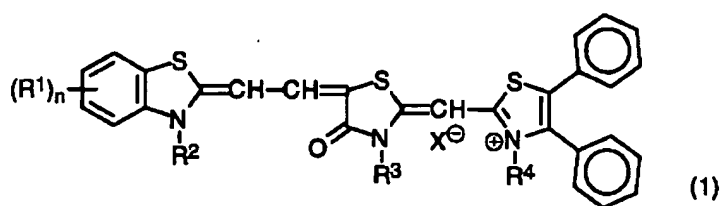
[Embodiment of the Invention] The optical information record medium (an optical disk may be called) of this invention has a recording layer containing the coloring matter compound which can record information by the exposure of a laser beam on a transparent disc-like substrate. And both reflection factors [as opposed to the laser beam of the wavelength of the range of 390-440nm and the laser beam of the wavelength of the range of 620-690nm in a recording layer] are 20% or more, the absolute value k of the real part n of the complex index of refraction of a recording layer and its imaginary part is $n \geq 1.8$, respectively, and it is characterized by being formed so that the relation of $0.02 < k < 0.5$ may be filled. Specifically, a coloring matter compound is selected and used so that the optical property of a recording layer may fill the above relation.

[0021] Generally complex index of refraction n_0 is given by the formula of $n_0 = n - ik$ (n : a refractive index, k : extinction coefficient). And the complex index of refraction of the recording layer containing a coloring matter compound changes with the wavelength of the laser beam to be used. In the optical information record medium of this invention, since a laser beam with a wavelength of 620-690nm (preferably 630-660nm) and the laser beam of the wavelength of the range of 390-440nm are used, it is adjusted so that a recording layer may fill the above-mentioned relational expression to the laser beam of these two wavelength regions. And in order to obtain better sensibility and for the optical information record medium of this invention to show the outstanding recording characteristic, it is desirable that k is in the range of $0.02 \leq k \leq 0.3$ (still more preferably $0.04 \leq k \leq 0.25$, especially preferably $0.06 \leq k \leq 0.2$) to the laser beam of the wavelength of the range of 620-690nm. Moreover, it is desirable that k is in the range of $0.03 \leq k \leq 0.3$ (still more preferably $0.04 \leq k \leq 0.25$, especially preferably $0.05 \leq k \leq 0.2$) to the laser beam of the wavelength of the range of 390-440nm. It is desirable that n is, on the other hand, filling the relation of $n \geq 2.0$ (still more preferably $n \geq 2.2$, especially preferably $n \geq 2.5$) to the wavelength region of the two above-mentioned laser beams in order to give a bigger modulation factor in reproducing characteristics.

[0022] Although the coloring matter compound used for a recording layer will not be limited especially if the optical property of a recording layer fills the above relation, it is desirable that it is what can use subabsorption of the absorption curve to the wavelength region of the laser beam of the range of 390-440nm. For example, as for the coloring matter compound used for this invention, in the absorption curve, it is desirable that it is what has at least two or more absorption-maximum wavelength, and has an edge by the side of the long wavelength of the subabsorption in the wavelength region of the laser beam of the range of 390-440nm. that is, it is desirable that a coloring matter compound is what has the maximum wave length of that subabsorption in a short wavelength side further rather than the wavelength region of the laser beam by the side of short wavelength (the maximum wave length of subabsorption of a coloring matter compound is further shifted to the short wavelength side rather than the wavelength region of the laser beam by the side of short wavelength -- this gap is generally in the range of $\sim 20\text{nm}$). as a desirable coloring matter compound with such an absorption curve -- for example, the following general formula -- the loader cyanine compound [(1 / [the semantics of the notation in a formula is) as aforementioned]] shown especially by the following formula (2) can be mentioned.

[0023]

[Formula 4]



[0024] Drawing 1 shows the absorption spectrum (absorption curve) in the wavelength region of the blue of the above-mentioned coloring matter compound or a purple-blue color - red. For example, to the laser beam with a wavelength of 408nm (purple-blue color) used in the example of this invention so that it might mention later, record playback can be performed by using the subabsorption maximum of about 390nm of the above-mentioned coloring matter compound (subabsorption peak). On the other hand, to a laser beam with a wavelength of 638nm (red), record playback can be similarly performed using the main absorption maximum of 600nm of the coloring matter compound (the main absorption peak).

[0025] Next, the manufacturing method of the optical information record medium of this invention which prepared on the substrate the recording layer which has the above optical properties is explained. The optical information record medium of this invention is manufactured by preparing a recording layer on a substrate. The optical information record medium of this invention can take various configurations. The configuration which has a recording layer and a reflecting layer on a transparent disc-like substrate at this order as a configuration which can be taken, for example, The configuration which has a recording layer, a reflecting layer, and a protective layer on this disc-like substrate at this order, On this disc-like substrate, or a recording layer and a reflecting layer, and two layered products in which the protective layer was further prepared by the request The thing of a configuration of having joined by the adhesives layer so that a recording layer side might turn into the inside, respectively, or the thing of a configuration of having joined similarly this layered product and the disc-like protective group plate (reflecting layers other than a recording layer etc. being prepared in this substrate) so that a recording layer side might turn into the inside can be mentioned. In these configurations, a laser beam is irradiated from a transparent substrate side.

[0026] Moreover, it is also possible to take the configuration which has in order a configuration [which has in order a configuration / which has a reflecting layer, a recording layer, and a protective layer for an optical information record medium in order on a disc-like substrate /, disc-like substrate, and adhesives layer, a disc-like substrate, a reflecting layer, a recording layer and a protective layer] or protective layer, recording layer, reflecting layer, disc-like substrate, and adhesives layer, a disc-like substrate, a reflecting layer, a recording layer, and a protective layer. In these configurations, a laser beam is irradiated from a protective layer side. In addition, in these configurations, a disc-like substrate does not need to be transparent. As for the optical information record medium of this invention, it is desirable that it is the mode which irradiates a laser beam from said substrate side. Below, taking the case of the optical information record medium of a configuration of having only a recording layer, the manufacturing method of the optical information record medium of this invention is explained in full detail on a transparent disc-like substrate.

[0027] A substrate can be chosen as arbitration from various kinds of ingredients used as a substrate of the conventional optical information record medium. As a substrate ingredient, vinyl chloride system resin; epoxy resin; amorphous polyolefine, polyester, etc., such as acrylic resin; polyvinyl chlorides, such as glass; polycarbonate; polymethylmethacrylate, and a vinyl chloride copolymer, can be

mentioned, and they may be used together by request, for example. In addition, these ingredients can be used as a substrate which has rigidity as the shape of a film. In the above-mentioned ingredient, points, such as moisture resistance, dimensional stability, and a price, to a polycarbonate is desirable.

[0028] It is desirable that the pre groove of a fixed track pitch is formed in the near front face in which the recording layer of the above-mentioned substrate is prepared. Although it is also possible to set it as 0.5-1.0 micrometers (still more preferably 0.6-0.9 micrometers) so that the track pitch formed in the conventional DVD-R may be suited for example, according to the laser beam (record light) of the range of 390-440nm, the track pitch of the pre groove formed on the substrate of the optical information record medium of this invention can be set up still more narrowly, and, thereby, can increase recording density. Thus, as for the track pitch of the pre groove doubled with the laser beam of short wavelength, it is desirable that it is in the range of 0.25-0.7 micrometers (still more preferably 0.3-0.55 micrometers, especially preferably 0.35-0.50 micrometers).

[0029] As for a pre groove, it is desirable that the side attachment wall inclines at an angle of the range of 55-80 degrees (still more preferably 60-80 degrees). Here, the include angle formed in respect of being level on extension of the straight line which connects the point on the side attachment wall of the slot in 10% of location of this depth of flute and the point on the side attachment wall of the slot in 50% of location of this depth of flute from the base of a pre groove (concave slot), and the base of a concave slot is meant as whenever [tilt-angle / of a side attachment wall]. Thus, it becomes possible to be able to control a cross talk, even if the track pitch of a pre groove becomes narrow, and to suppress the rise of a jitter value by making whenever [tilt-angle / of the side attachment wall of a pre groove] into a sudden include angle. In addition, such a pre groove of a configuration can form a substrate using La Stampa for resin molding (metal mold) processed so that it might have the side attachment wall of whenever [predetermined tilt-angle] beforehand, injection molding or in case it extrudes and casts.

[0030] Also in the shape of a quirk of a pre groove (depth and width of face), it can set up narrowly compared with DVD-R according to the laser beam (record light) of the range of 390-440nm. As for the depth of a pre groove, it is desirable that it is in the range of 30-170nm (still more preferably 50-140nm, especially preferably 65-130nm), and, as for the width of face (half-value width) of a pre groove, it is desirable that it is in the range of 65-300nm (still more preferably 95-260nm, especially preferably 130-230nm).

[0031] Undercoat may be prepared in the near substrate front face in which a recording layer is prepared for the purpose, such as an improvement of smoothness, improvement in adhesive strength, and deterioration prevention of a recording layer. As an ingredient of undercoat, for example Polymethylmethacrylate, an acrylic acid and a methacrylic-acid copolymer, A styrene maleic anhydride copolymer, polyvinyl alcohol, N-methylol acrylamide, A styrene vinyltoluene copolymer, Krol sulfonation polyethylene, A nitrocellulose, a polyvinyl chloride, chlorinated polyolefins, polyester, Surface treatment agents, such as high polymer [, such as polyimide vinyl acetate and a vinyl chloride copolymer, an ethylene-vinylacetate copolymer, polyethylene, polypropylene, and a polycarbonate,]; and a silane coupling agent, can be mentioned. Undercoat can be formed by applying this coating liquid to a substrate front face using the applying methods, such as a spin coat, a DIP coat, and an extrusion coat, after dissolving or distributing the above-mentioned matter to a suitable solvent and preparing coating liquid. Generally the thickness of undercoat is in the range of 0.005-20 micrometers, and the range of it is 0.01-10 micrometers preferably.

[0032] Formation of a pre groove may be performed by preparing a pre groove layer. As an ingredient of a pre groove layer, the mixture of a kind of monomer of the monoester of an acrylic acid, diester, triester, and the tetra-ester (or oligomer) and a photopolymerization initiator can be used at least. After formation of a pre groove layer applies the mixed liquor which consists of above-mentioned acrylic ester and an above-mentioned polymerization initiator on the matrix (La Stampa) first made by the precision and carries a substrate on this coating liquid layer further, for example, it stiffens a spreading layer and makes a substrate and a spreading layer fix by irradiating ultraviolet rays through a substrate or a matrix. Subsequently, a substrate can be obtained by exfoliating from a matrix. Generally, the thickness of a pre groove layer is in the range of 0.03-70 micrometers, and the range of it is 0.06-35 micrometers

preferably.

[0033] On a substrate, a coloring matter compound content recording layer is prepared. Formation of a recording layer can be performed by drying, after dissolving said specific coloring matter compound in a solvent, preparing coating liquid for example, applying this coating liquid to that front face in which said pre groove of a substrate is formed and forming a paint film. adding a fading inhibitor on the occasion of preparation of coating liquid -- a binder can also be further added by request.

[0034] As an example of the solvent of the coating liquid for record stratification, ester; methyl ethyl ketones, such as butyl acetate and a cellosolve acetate, Ketones, such as a cyclohexanone and methyl isobutyl ketone; Dichloromethane, Hydrocarbons [, such as chlorinated-hydrocarbon; dimethylformamide /, such as an amide; cyclohexane], such as 1,2-dichloroethane and chloroform; A tetrahydrofuran, The ether, such as ethyl ether and dioxane; Ethanol, n-propanol, Fluorine system solvents, such as alcoholic;2, such as isopropanol, n-butanol, and diacetone alcohol, 2 and 3, and 3-tetra-FURORO propanol; Ethylene glycol monomethyl ether, Glycol ether, such as ethylene glycol monoethyl ether and propylene glycol monomethyl ether, can be mentioned. The above-mentioned solvent can be used combining independent or two sorts or more in consideration of the solubility of the compound to be used. In coating liquid, you may add [for the purpose of various kinds of additives such as an antioxidant, UV absorbent, a plasticizer, and lubricant,] further.

[0035] As a typical example of a fading inhibitor, a nitroso compound, a metal complex, diammonium salt, an aminium salt, etc. can be mentioned. These examples are indicated by each official report, such as JP,2-300288,A, 3-224793, or 4-146189. the case where a fading inhibitor is used -- the amount used - - the amount of a coloring matter compound -- receiving -- usually -- 0.1 - 50% of the weight of the range -- it is -- desirable -- 0.5 - 45% of the weight of the range -- further -- desirable -- 3 - 40% of the weight of the range -- it is 5 - 25% of the weight of the range especially.

[0036] As an example of a binder, for example Gelatin, a cellulosic, a dextran, Natural organic polymeric-materials [, such as rosin and rubber,]; and polyurethane, polyethylene, Hydrocarbon system resin, such as polypropylene, polystyrene, and a polyisobutylene; A polyvinyl chloride, Vinyl system resin, such as a polyvinylidene chloride and a polyvinyl chloride polyvinyl acetate copolymer; Polymethylacrylate, Acrylic resin, such as a polymethyl methacrylate; synthetic organic macromolecules, such as an initial condensate of thermosetting resin, such as polyvinyl alcohol, chlorinated polyethylene, an epoxy resin, butyral resin, a rubber derivative, and phenol-formaldehyde resin, can be mentioned. the case where a binder is used together as an ingredient of a recording layer -- the amount of the binder used -- the coloring matter compound 100 weight section -- receiving -- 0.2 - 20 weight section -- desirable -- 0.5 - 10 weight section -- it is 1 - 5 weight section still more preferably. Thus, generally the concentration of the coloring matter compound in the coating liquid prepared is in 0.01 - 10% of the weight of the range, and is in 0.1 - 5% of the weight of the range preferably.

[0037] As the method of application, a spray method, a spin coat method, a dip method, the roll coat method, the blade coat method, the doctor roll method, screen printing, etc. can be mentioned. A monolayer or multistory are sufficient as a recording layer. Generally the thickness (average thickness after desiccation) of a recording layer is in the range of 10-350nm, and the range of it is 30-250nm preferably. the case of the optical information record medium of this invention -- the thickness in the pre groove of a recording layer -- desirable -- the range of 50-200nm -- it is -- further -- desirable -- the range of 60-150nm -- it is the range of 65-120nm especially preferably. moreover, the thickness of a land -- desirable -- the range of 30-150nm -- it is -- further -- desirable -- the range of 40-120nm -- it is the range of 50-100nm especially preferably.

[0038] According to the above process, the optical information record medium of this invention which has a recording layer on a substrate can be manufactured.

[0039] The case where a reflecting layer and a protective layer are prepared is explained below. Generally a reflecting layer is prepared on a recording layer or a substrate for the purpose of improvement in the reflection factor at the time of informational playback. The light reflex nature matter which is the ingredient of a reflecting layer is matter with the high reflection factor to a laser beam. As the example Mg, Se, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, A metal and semimetal, or stainless steel, such as

W, Mn, Re, Fe, Co, nickel, Ru, Rh, Pd, Ir, Pt, Cu, Ag, Au, Zn, Cd, aluminum, Ga, In, Si, germanium, Te, Pb, Po, Sn, and Bi, can be mentioned. Things desirable [among these] are Cr, nickel, Pt, Cu, Ag, Au, aluminum, and stainless steel. These matter may be used independently, or is two or more sorts of combination, or may be used as an alloy. It is the alloy which contains Au, Ag, and these metals preferably especially. A reflecting layer can form for example, the above-mentioned reflexivity matter on a recording layer or a substrate vacuum evaporation, sputtering, or by carrying out ion plating. the thickness of a reflecting layer -- general -- the range of 5-500nm -- it is -- desirable -- the range of 10-350nm -- it is the range of 30-200nm still more preferably.

[0040] A protective layer is prepared in order to protect a recording layer and a reflecting layer physically and chemically. as the ingredient used for a protective layer -- SiO, SiO₂, MgF₂, SnO₂, and Si₃N₄ etc. -- organic substances, such as mineral matter, thermoplastics, thermosetting resin, and UV hardenability resin, can be mentioned. As for a protective layer, being formed by resin is desirable. When preparing a protective layer on a reflecting layer, a protective layer can be formed by laminating the film obtained with the extrusion of plastics on a reflecting layer through a glue line. Or a protective layer may be prepared by approaches, such as vacuum deposition, sputtering, and spreading. Moreover, in the case of thermoplastics and thermosetting resin, after dissolving these in a suitable solvent and preparing coating liquid, this coating liquid can be applied and a protective layer can be formed by drying. After dissolving in a solvent remaining as it is or suitable in the case of UV hardenability resin and preparing coating liquid, this coating liquid can be applied, and a protective layer can be formed by irradiating UV light and stiffening it. In these coating liquid, you may add [for the purpose of various additives, such as an antistatic agent, an antioxidant, and UV absorbent,] further. Generally the thickness of a protective layer is in the range of 0.05-70 micrometers.

[0041] The optical information record medium which has two recording layers can be manufactured by preparing two layered products which prepared the protective layer by the recording layer, the reflecting layer, and request on the substrate, and sticking with adhesives etc. so that each recording layer may serve as the inside. moreover, the obtained layered product, the substrate of this layered product, and abbreviation -- the optical information record medium which has a recording layer only in one side can be manufactured by sticking the same disc-like protective group plate of a dimension with adhesives etc. so that the recording layer may serve as the inside. UV hardenability resin which used adhesion for formation of said protective layer, and synthetic adhesives -- or it can carry out again using a double-sided tape etc. Thus, the adhesives layer formed is usually prepared by the thickness of the range of 0.05-70 micrometers (preferably 3-50 micrometers).

[0042] The informational record playback approach using the optical information record medium of this invention is enforced as follows, for example. Rotating an optical information record medium with a constant predetermined linear velocity (in CD format, it is 1.2-1.4m/second 1X) or a constant predetermined angular velocity, the laser beam for record of semiconductor laser light etc. is condensed through optical system from a substrate or protective layer side, and a recording layer is irradiated. Information is recorded by the exposure part of a recording layer absorbing the light, carrying out a temperature rise locally, and a physical or chemical change arising, and changing the optical property by the exposure of a laser beam. In this invention, the semi-conductor laser beam which has the oscillation wavelength of the blue glow of the semi-conductor laser beam which has the oscillation wavelength of the red light of the range of 620-690nm, and the range of 390-440nm, or purple-blue colored light as a record light is used. Moreover, as for record light, it is desirable that NA is condensed through the optical system of 0.55-0.7.

[0043] Playback of the information recorded as mentioned above irradiates the above-mentioned semiconductor laser light from a substrate or protective layer side, rotating the optical information record medium after record with a constant predetermined linear velocity, and is performed by detecting the reflected light. Even if a laser beam with the oscillation wavelength of which the above-mentioned range is used for the optical information record medium of this invention, record playback of it can be carried out. It is desirable to use the record playback approach reproduced using the semi-conductor laser beam which records in this invention using the semi-conductor laser beam which has the

oscillation wavelength of blue or a purple-blue color, and has red oscillation wavelength. There is an advantage reproducible using the record regeneration system already used widely as an object for DVD-R without using the regeneration system of the dedication which has the same oscillation wavelength as record light for the optical information record medium which recorded and manufactured image information by using this approach, using blue or a purple-blue color laser beam as for example, a record light.

[0044]

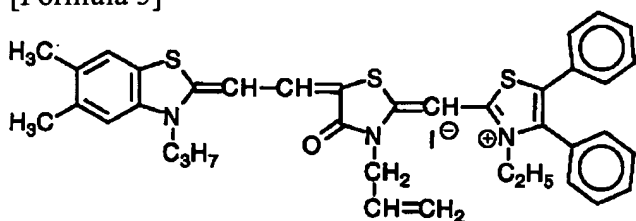
[Example] Below, the example and the example of a comparison of this invention are indicated.

[0045] [Example 1]

The disc-like resin substrate (0.6mm in the diameter of 120mm, the bore of 15mm, thickness) made from a polycarbonate (resin trade name: the panlight AD 5503 and Teijin, Ltd.) was produced using the injection molding machine which contains La Stampa produced so that it might become the production predetermined track pitch of a disc-like substrate, and a slot (pre groove). The track pitch of the concave slot (pre groove) of the obtained resin substrate The width of face of 90nm and a slot is 0.48 micrometers, and the depth of flute is whenever [190nm and tilt-angle / of the side attachment wall of a slot] (with extension of the straight line which connects the point on the side attachment wall of the slot in 10% of location of the depth of flute, and the point on the side attachment wall of the slot in 50% of location of the depth of flute from the base of a slot). The include angle formed in respect of being level on the base of a concave slot was 60 degrees. Measurement of these configurations was performed using AFM.

[0046]

[Formula 5]



[0047] It dissolved into 2, 2, 3, and 3-tetrafluoro-1-propanol, and the coating liquid for record stratification was prepared so that the concentration in the solution of the above-mentioned coloring matter might become 1 % of the weight. This coating liquid was applied to the front face in which that pre groove of the disc-like polycarbonate substrate obtained above is prepared with the spin coat method, it dried, the recording layer (thickness in a groove: 120nm, thickness:80nm of a land) was formed, and the optical information record medium (optical disk) according to this invention was manufactured.

[0048] [Evaluation as an optical information record medium]

(1) Using the following record regenerative apparatus, record power was changed to 3-10mW with a constant linear velocity of 3.5m/second, and the signal of a square wave with a frequency of 1MHz was recorded on the obtained optical disk by the optimal record power.

Record regenerative apparatus: DDU1000 (pulse tech company make)

laser: -- semiconductor laser pickup NA:0.6 rim intensity: with dispatch wavelength with a purple-blue color of 408nm -- the tangential direction 0.33 radial-direction deviation beam of 0.21 yen was used, and it carried out by a focus's using the knife-edge method and tracking using the push pull method. The refractive index n of the recording layer obtained to the laser beam with a wavelength of 408nm was 2.2, and the extinction coefficient k was 0.05.

[0049] The record signal was reproduced by 0.5mW laser power after record using the laser beam for record, and the laser beam of the same wavelength, and the modulation factor was measured. The modulation factor set to A the maximal value of the reflected light level of a direct-current playback wave when reproducing the signal recorded on the above-mentioned conditions, set the minimal value to B, set reflected light level when performing groove tracking at the non-Records Department to R, and

asked for it from the following formula.

Modulation factor (%) = $(A-B) / R \times 100\%$, consequently 62% of modulation factor was obtained.

[0050] (2) The semiconductor laser which has dispatch wavelength with a red of 638nm in the above-mentioned record regenerative apparatus was carried, and the signal was recorded on the optical disk like the above (1). The refractive index n of the recording layer obtained to the laser beam with a wavelength of 638nm was 2.3, and the extinction coefficient k was 0.1. Then, it reproduced using the laser beam of the same wavelength, and the modulation factor was measured by the same approach. Consequently, 65% of modulation factor was obtained.

[0051] (3) After recording a signal using semiconductor laser with dispatch wavelength with a purple-blue color of 408 above-mentionednm, when the signal recorded using semiconductor laser with dispatch wavelength with a red of 638nm was reproduced, the signal was reproducible in high resolution.

[0052]

[Effect of the Invention] By using the optical information record medium according to this invention, record playback is possible in the wavelength region of the laser beam of the laser beam for DVD-R and blue, or a purple-blue color. And the optical information record medium according to this invention shows good record reproducing characteristics in the laser beam of both wavelength regions. Therefore, the information recorded using the laser beam of blue or a purple-blue color is reproducible using the laser beam for DVD-R. Moreover, by using the laser beam of blue or a purple-blue color, it becomes more recordable [high density] and the optical, still bigger information record medium of storage capacity can be manufactured.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the optical information record medium [reading / information / record medium / record and reading] by the exposure of a laser beam. Furthermore, this invention relates to the optical information record medium [reading / information / record medium / record and reading], and the optical information record playback approach by the exposure of a laser beam in two wavelength regions in detail.

[0002]

[Description of the Prior Art] The added type light information record medium (the so-called CD-R type of optical disk) of a postscript which can record the information only for 1 time is put in practical use by the exposure of a laser beam. The optical disk of a CD-R mold has the structure which generally prepared the recording layer which consists of coloring matter, and the reflecting layer which consists of a metal on the disc-like substrate at this order, and was established so that the protective layer which consists of resin further might cover this on a reflecting layer by spreading.

[0003] As an optical disk which can perform record playback using the laser beam of short wavelength from the optical disk of a CD-R mold, the postscript mold DVD (digital video disc: DVD-R) is proposed (for example, the "Nikkei new-medium" separate volume "DVD", 1995 issue). As optical De Dis of a DVD-R mold, the guide rail for the tracking of the laser beam irradiated (pre groove) compared with optical ISUKU of a CD-R mold below one half and on the transparent disc-like substrate with which it was formed narrowly The recording layer which consists of organic coloring matter, and the layered product of two sheets which usually comes to prepare a reflecting layer and a protective layer further on a recording layer The thing of a configuration of having replaced with the disc-like guard plate the one the thing of the structure which carries out this each recording layer inside, and was stuck with adhesives, or in the layered product which consists of two above-mentioned sheets, and having prepared the recording layer, the reflecting layer, and the protective layer only in one substrate in order is common. Compared with the optical disk of a CD-R mold, record of capacity of this type of optical disk is enabled six to 8 times.

[0004] Writing (record) and reading (playback) of the information on the above-mentioned CD-R or DVD-R are performed by irradiating visible laser light (CD-R being 750-800nm, and DVD-R being usually the laser beam of the range of 600-700nm wavelength). That is, if the above-mentioned laser beam is irradiated at an optical disk, informational record will be performed, when the exposure part of a coloring matter recording layer absorbs the light, a temperature rise is carried out locally, it changes physically or chemically (for example, generation of a pit etc.) and the optical property changes. On the other hand, reading of information is also performed by usually irradiating the laser beam for record, and the laser beam of the same wavelength at an optical disk, and is carried out by detecting the difference in the reflection factor of the part (record part by generation of a pit etc.) where the optical property of a coloring matter recording layer changed, and the part (non-recorded part) not changing.

[0005] Recently, the demand of the mass record medium for recording image information cheaply

simple is increasing with the rapid spread of networks, such as the Internet, or Hi-Vision TV. To such a demand, by using the laser beam of short wavelength further rather than DVD-R, recording density is raised and development of the optical disk equipped with bigger storage capacity is furthered. For example, in the optical information record medium of a configuration of that the light reflex layer formed in JP,11-53758,A from the recording layer containing organic coloring matter and silver, or its alloy was prepared, the record playback approach of performing informational record playback is indicated by irradiating a laser beam with a wavelength of 530nm or less towards a light reflex layer side from a recording layer side. The information record playback approach of specifically performing informational record playback to the optical disk using metal azo system coloring matter, kino FUTARON system coloring matter, or TORIMECHIN cyanine dye as coloring matter of a recording layer by irradiating the semiconductor laser light of blue (wavelength of 410nm) or a bluish green color (wavelength of 515nm) is proposed.

[0006] Moreover, it is the recording layer which mixed two or more coloring matter, and in JP,58-56239,A, it has 80% or more of rate of light absorption on all the wavelength of 400-900nm, and the optical recording medium which enabled it to correspond also to modification of a laser light source is indicated. To JP,10-181211,A, record playback is possible at 620-690nm, and the optical recording medium for DVD-R with which n has the cyanine dye content recording layer 0.01 to 0.45 and whose maximum absorption peak wavelength 1.6-4.0 μ m are 500-655nm is indicated.

[0007] The optical information record medium which has a recording layer containing two or more sorts of cyanine dye whose absorption maximums are 600-900nm, and the azo dye whose absorption maximum is 350-600nm in the patent official report (registration) No. 2925121 and whose lightfastness improved is indicated. Optical information record media, such as CD-R which can reproduce 630-680nm information, or DVD-R, are indicated possible [informational record and playback] in the wavelength range of 770-830nm by JP,10-162429,A. By the recording layer which specified 630-650nm [780nm and] n and k, respectively, it corresponds to Orange Book specification and the optical information record medium whose record playback with short wavelength was enabled is indicated by JP,9-66671,A.

[0008]

[Problem(s) to be Solved by the Invention] By short-wavelength-izing record wavelength further like a publication to above-mentioned JP,11-53758,A, the design of the optical information record medium of bigger storage capacity is attained. And although it usually reproduces using the laser beam for record, and the laser beam of the almost same wavelength region using the record regeneration system only for short wavelength, the recorded image information is convenient if the image information recorded with short wavelength as mentioned above is reproducible using the existing record regeneration system used as an object for DVD-R.

[0009] The technical problems of this invention are the laser beam of the wavelength region of short wavelength, and offering especially the optical information record medium which can record informational by the laser beam of the wavelength of the range of 390-440nm more nearly further than the record playback wavelength field for DVD-R, and this. Moreover, the technical problem of this invention is also offering the optical information record medium and the optical information record playback approach of doing, although the information recorded with the above short wavelength is reproduced using the existing record regeneration system.

[0010]

[Means for Solving the Problem] It was found out that the optical information record medium in which good record reproducing characteristics are shown by research of this invention person to the laser beam of the laser beam for DVD-R and blue, or a purple-blue color by setting up the optical constant of the recording layer of an optical information record medium so that it may become the specific range can be manufactured. It was found out by using the specific loader cyanine compound which specifically has an absorption curve which has absorption-maximum wavelength in a short wavelength side rather than those wavelength regions to the wavelength region of the two above laser beams, respectively as a record ingredient that the optical information record medium made into the purpose can be

manufactured.

[0011] This invention is an optical information record medium which has on a substrate a recording layer containing the coloring matter compound which can record the information by the exposure of a laser beam. A reflection factor [as opposed to each of the laser beam of the wavelength of the range of 390-440nm and the laser beam of the wavelength of the range of 620-690nm in this recording layer] is 20% or more (30% or more preferably). It is in the optical information record medium which it is 40% or more still more preferably, and the absolute value k of the real part n of the complex index of refraction of this recording layer and its imaginary part is $n \geq 1.8$, and is characterized by being formed so that the relation of $0.02 < k < 0.5$ may be filled.

[0012] Moreover, after this invention irradiates the laser beam of the wavelength of the range of 390-440nm and records information on the above optical information record media of a configuration, it is also in the optical information record playback approach characterized by irradiating the laser beam of the wavelength of the range of 620-690nm, and reproducing information.

[0013] As for the optical information record medium of this invention, and the optical information record playback approach, it is desirable that they are the following modes.

(1) The real part n of the complex index of refraction of a recording layer to the laser beam of the wavelength of the range of 390-440nm and the laser beam of the wavelength of the range of 620-690nm is $n \geq 2.0$ (still more preferably $n \geq 2.1$, especially preferably $n \geq 2.2$).

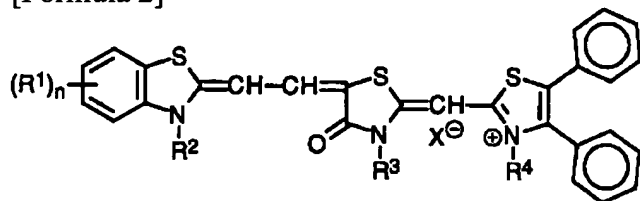
(2) The optical information record medium currently formed so that a recording layer may fill the relation of $0.05 \leq k \leq 0.3$ (still more preferably $0.08 \leq k \leq 0.25$, especially preferably $0.1 \leq k \leq 0.2$) to the laser beam of the wavelength of the range of 620-690nm.

[0014] (3) The optical information record medium currently formed so that a recording layer may fill the relation of $0.03 \leq k \leq 0.3$ (still more preferably $0.04 \leq k \leq 0.25$, especially preferably $0.05 \leq k \leq 0.2$) to the laser beam of the wavelength of the range of 390-440nm.

(4) that in which a coloring matter compound has at least two or more absorption-maximum wavelength in the absorption curve -- it is -- the long wave of the subabsorption -- the optical information record medium which has an edge by the side of merit in the wavelength region of the laser beam of the range of 390-440nm.

(5) Optical information record medium whose coloring matter compound is a loader cyanine compound shown by the following general formula : [0015]

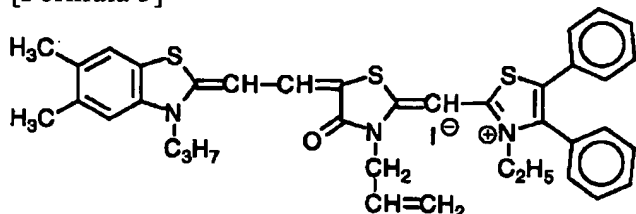
[Formula 2]



[0016] [in the above-mentioned general formula, the carbon number of R1, R2, R3, and R4 is the alkyl group of the saturation of 1-6, or partial saturation mutually-independent, and n is the integer of 1-4, and X^- is an organic or inorganic counter ion].

[0017] (6) Optical information record medium whose coloring matter compound is a loader cyanine compound shown by the following formula : [0018]

[Formula 3]



[0019] (7) The thickness of a recording layer is in a pre groove in the range of 50-200nm (preferably 60-150nm, especially preferably 65-120nm).

[0020]

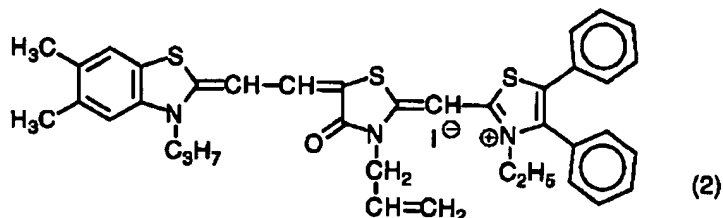
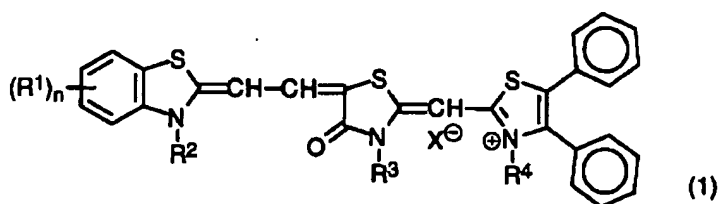
[Embodiment of the Invention] The optical information record medium (an optical disk may be called) of this invention has a recording layer containing the coloring matter compound which can record information by the exposure of a laser beam on a transparent disc-like substrate. And both reflection factors [as opposed to the laser beam of the wavelength of the range of 390-440nm and the laser beam of the wavelength of the range of 620-690nm in a recording layer] are 20% or more, the absolute value k of the real part n of the complex index of refraction of a recording layer and its imaginary part is $n \geq 1.8$, respectively, and it is characterized by being formed so that the relation of $0.02 < k < 0.5$ may be filled. Specifically, a coloring matter compound is selected and used so that the optical property of a recording layer may fill the above relation.

[0021] Generally complex index of refraction n_0 is given by the formula of $n_0 = n - ik$ (n : a refractive index, k : extinction coefficient). And the complex index of refraction of the recording layer containing a coloring matter compound changes with the wavelength of the laser beam to be used. In the optical information record medium of this invention, since a laser beam with a wavelength of 620-690nm (preferably 630-660nm) and the laser beam of the wavelength of the range of 390-440nm are used, it is adjusted so that a recording layer may fill the above-mentioned relational expression to the laser beam of these two wavelength regions. And in order to obtain better sensibility and for the optical information record medium of this invention to show the outstanding recording characteristic, it is desirable that k is in the range of $0.02 \leq k \leq 0.3$ (still more preferably $0.04 \leq k \leq 0.25$, especially preferably $0.06 \leq k \leq 0.2$) to the laser beam of the wavelength of the range of 620-690nm. Moreover, it is desirable that k is in the range of $0.03 \leq k \leq 0.3$ (still more preferably $0.04 \leq k \leq 0.25$, especially preferably $0.05 \leq k \leq 0.2$) to the laser beam of the wavelength of the range of 390-440nm. It is desirable that n is, on the other hand, filling the relation of $n \geq 2.0$ (still more preferably $n \geq 2.2$, especially preferably $n \geq 2.5$) to the wavelength region of the two above-mentioned laser beams in order to give a bigger modulation factor in reproducing characteristics.

[0022] Although the coloring matter compound used for a recording layer will not be limited especially if the optical property of a recording layer fills the above relation, it is desirable that it is what can use subabsorption of the absorption curve to the wavelength region of the laser beam of the range of 390-440nm. For example, as for the coloring matter compound used for this invention, in the absorption curve, it is desirable that it is what has at least two or more absorption-maximum wavelength, and has an edge by the side of the long wavelength of the subabsorption in the wavelength region of the laser beam of the range of 390-440nm. that is, it is desirable that a coloring matter compound is what has the maximum wave length of that subabsorption in a short wavelength side further rather than the wavelength region of the laser beam by the side of short wavelength (the maximum wave length of subabsorption of a coloring matter compound is further shifted to the short wavelength side rather than the wavelength region of the laser beam by the side of short wavelength -- this gap is generally in the range of $\sim 20\text{nm}$). as a desirable coloring matter compound with such an absorption curve -- for example, the following general formula -- the loader cyanine compound [(1 / [the semantics of the notation in a formula is) as aforementioned]] shown especially by the following formula (2) can be mentioned.

[0023]

[Formula 4]



[0024] Drawing 1 shows the absorption spectrum (absorption curve) in the wavelength region of the blue of the above-mentioned coloring matter compound or a purple-blue color - red. For example, to the laser beam with a wavelength of 408nm (purple-blue color) used in the example of this invention so that it might mention later, record playback can be performed by using the subabsorption maximum of about 390nm of the above-mentioned coloring matter compound (subabsorption peak). On the other hand, to a laser beam with a wavelength of 638nm (red), record playback can be similarly performed using the main absorption maximum of 600nm of the coloring matter compound (the main absorption peak).

[0025] Next, the manufacturing method of the optical information record medium of this invention which prepared on the substrate the recording layer which has the above optical properties is explained. The optical information record medium of this invention is manufactured by preparing a recording layer on a substrate. The optical information record medium of this invention can take various configurations. The configuration which has a recording layer and a reflecting layer on a transparent disc-like substrate at this order as a configuration which can be taken, for example, The configuration which has a recording layer, a reflecting layer, and a protective layer on this disc-like substrate at this order, On this disc-like substrate, or a recording layer and a reflecting layer, and two layered products in which the protective layer was further prepared by the request The thing of a configuration of having joined by the adhesives layer so that a recording layer side might turn into the inside, respectively, or the thing of a configuration of having joined similarly this layered product and the disc-like protective group plate (reflecting layers other than a recording layer etc. being prepared in this substrate) so that a recording layer side might turn into the inside can be mentioned. In these configurations, a laser beam is irradiated from a transparent substrate side.

[0026] Moreover, it is also possible to take the configuration which has in order a configuration [which has in order a configuration / which has a reflecting layer, a recording layer, and a protective layer for an optical information record medium in order on a disc-like substrate /, disc-like substrate, and adhesives layer, a disc-like substrate, a reflecting layer, a recording layer and a protective layer] or protective layer, recording layer, reflecting layer, disc-like substrate, and adhesives layer, a disc-like substrate, a reflecting layer, a recording layer, and a protective layer. In these configurations, a laser beam is irradiated from a protective layer side. In addition, in these configurations, a disc-like substrate does not need to be transparent. As for the optical information record medium of this invention, it is desirable that it is the mode which irradiates a laser beam from said substrate side. Below, taking the case of the optical information record medium of a configuration of having only a recording layer, the manufacturing method of the optical information record medium of this invention is explained in full detail on a transparent disc-like substrate.

[0027] A substrate can be chosen as arbitration from various kinds of ingredients used as a substrate of the conventional optical information record medium. As a substrate ingredient, vinyl chloride system resin; epoxy resin; amorphous polyolefine, polyester, etc., such as acrylic resin; polyvinyl chlorides, such as glass; polycarbonate; polymethylmethacrylate, and a vinyl chloride copolymer, can be

mentioned, and they may be used together by request, for example. In addition, these ingredients can be used as a substrate which has rigidity as the shape of a film. In the above-mentioned ingredient, points, such as moisture resistance, dimensional stability, and a price, to a polycarbonate is desirable.

[0028] It is desirable that the pre groove of a fixed track pitch is formed in the near front face in which the recording layer of the above-mentioned substrate is prepared. Although it is also possible to set it as 0.5-1.0 micrometers (still more preferably 0.6-0.9 micrometers) so that the track pitch formed in the conventional DVD-R may be suited for example, according to the laser beam (record light) of the range of 390-440nm, the track pitch of the pre groove formed on the substrate of the optical information record medium of this invention can be set up still more narrowly, and, thereby, can increase recording density. Thus, as for the track pitch of the pre groove doubled with the laser beam of short wavelength, it is desirable that it is in the range of 0.25-0.7 micrometers (still more preferably 0.3-0.55 micrometers, especially preferably 0.35-0.50 micrometers).

[0029] As for a pre groove, it is desirable that the side attachment wall inclines at an angle of the range of 55-80 degrees (still more preferably 60-80 degrees). Here, the include angle formed in respect of being level on extension of the straight line which connects the point on the side attachment wall of the slot in 10% of location of this depth of flute and the point on the side attachment wall of the slot in 50% of location of this depth of flute from the base of a pre groove (concave slot), and the base of a concave slot is meant as whenever [tilt-angle / of a side attachment wall]. Thus, it becomes possible to be able to control a cross talk, even if the track pitch of a pre groove becomes narrow, and to suppress the rise of a jitter value by making whenever [tilt-angle / of the side attachment wall of a pre groove] into a sudden include angle. In addition, such a pre groove of a configuration can form a substrate using La Stampa for resin molding (metal mold) processed so that it might have the side attachment wall of whenever [predetermined tilt-angle] beforehand, injection molding or in case it extrudes and casts.

[0030] Also in the shape of a quirk of a pre groove (depth and width of face), it can set up narrowly compared with DVD-R according to the laser beam (record light) of the range of 390-440nm. As for the depth of a pre groove, it is desirable that it is in the range of 30-170nm (still more preferably 50-140nm, especially preferably 65-130nm), and, as for the width of face (half-value width) of a pre groove, it is desirable that it is in the range of 65-300nm (still more preferably 95-260nm, especially preferably 130-230nm).

[0031] Undercoat may be prepared in the near substrate front face in which a recording layer is prepared for the purpose, such as an improvement of smoothness, improvement in adhesive strength, and deterioration prevention of a recording layer. As an ingredient of undercoat, for example Polymethylmethacrylate, an acrylic acid and a methacrylic-acid copolymer, A styrene maleic anhydride copolymer, polyvinyl alcohol, N-methylol acrylamide, A styrene vinyltoluene copolymer, Krol sulfonation polyethylene, A nitrocellulose, a polyvinyl chloride, chlorinated polyolefins, polyester, Surface treatment agents, such as high polymer [, such as polyimide vinyl acetate and a vinyl chloride copolymer, an ethylene-vinylacetate copolymer, polyethylene, polypropylene, and a polycarbonate,]; and a silane coupling agent, can be mentioned. Undercoat can be formed by applying this coating liquid to a substrate front face using the applying methods, such as a spin coat, a DIP coat, and an extrusion coat, after dissolving or distributing the above-mentioned matter to a suitable solvent and preparing coating liquid. Generally the thickness of undercoat is in the range of 0.005-20 micrometers, and the range of it is 0.01-10 micrometers preferably.

[0032] Formation of a pre groove may be performed by preparing a pre groove layer. As an ingredient of a pre groove layer, the mixture of a kind of monomer of the monoester of an acrylic acid, diester, triester, and the tetra-ester (or oligomer) and a photopolymerization initiator can be used at least. After formation of a pre groove layer applies the mixed liquor which consists of above-mentioned acrylic ester and an above-mentioned polymerization initiator on the matrix (La Stampa) first made by the precision and carries a substrate on this coating liquid layer further, for example, it stiffens a spreading layer and makes a substrate and a spreading layer fix by irradiating ultraviolet rays through a substrate or a matrix. Subsequently, a substrate can be obtained by exfoliating from a matrix. Generally, the thickness of a pre groove layer is in the range of 0.03-70 micrometers, and the range of it is 0.06-35 micrometers

preferably.

[0033] On a substrate, a coloring matter compound content recording layer is prepared. Formation of a recording layer can be performed by drying, after dissolving said specific coloring matter compound in a solvent, preparing coating liquid for example, applying this coating liquid to that front face in which said pre groove of a substrate is formed and forming a paint film. adding a fading inhibitor on the occasion of preparation of coating liquid -- a binder can also be further added by request.

[0034] As an example of the solvent of the coating liquid for record stratification, ester; methyl ethyl ketones, such as butyl acetate and a cellosolve acetate, Ketones, such as a cyclohexanone and methyl isobutyl ketone; Dichloromethane, Hydrocarbons [, such as chlorinated-hydrocarbon; dimethylformamide /, such as an amide; cyclohexane], such as 1,2-dichloroethane and chloroform; A tetrahydrofuran, The ether, such as ethyl ether and dioxane; Ethanol, n-propanol, Fluorine system solvents, such as alcoholic;2, such as isopropanol, n-butanol, and diacetone alcohol, 2 and 3, and 3-tetra-FURORO propanol; Ethylene glycol monomethyl ether, Glycol ether, such as ethylene glycol monoethyl ether and propylene glycol monomethyl ether, can be mentioned. The above-mentioned solvent can be used combining independent or two sorts or more in consideration of the solubility of the compound to be used. In coating liquid, you may add [for the purpose of various kinds of additives such as an antioxidant, UV absorbent, a plasticizer, and lubricant,] further.

[0035] As a typical example of a fading inhibitor, a nitroso compound, a metal complex, diammonium salt, an aminium salt, etc. can be mentioned. These examples are indicated by each official report, such as JP,2-300288,A, 3-224793, or 4-146189. the case where a fading inhibitor is used -- the amount used - - the amount of a coloring matter compound -- receiving -- usually -- 0.1 - 50% of the weight of the range -- it is -- desirable -- 0.5 - 45% of the weight of the range -- further -- desirable -- 3 - 40% of the weight of the range -- it is 5 - 25% of the weight of the range especially.

[0036] As an example of a binder, for example Gelatin, a cellulosic, a dextran, Natural organic polymeric-materials [, such as rosin and rubber,]; and polyurethane, polyethylene, Hydrocarbon system resin, such as polypropylene, polystyrene, and a polyisobutylene; A polyvinyl chloride, Vinyl system resin, such as a polyvinylidene chloride and a polyvinyl chloride polyvinyl acetate copolymer; Polymethylacrylate, Acrylic resin, such as a polymethyl methacrylate; synthetic organic macromolecules, such as an initial condensate of thermosetting resin, such as polyvinyl alcohol, chlorinated polyethylene, an epoxy resin, butyral resin, a rubber derivative, and phenol-formaldehyde resin, can be mentioned. the case where a binder is used together as an ingredient of a recording layer -- the amount of the binder used -- the coloring matter compound 100 weight section -- receiving -- 0.2 - 20 weight section -- desirable -- 0.5 - 10 weight section -- it is 1 - 5 weight section still more preferably. Thus, generally the concentration of the coloring matter compound in the coating liquid prepared is in 0.01 - 10% of the weight of the range, and is in 0.1 - 5% of the weight of the range preferably.

[0037] As the method of application, a spray method, a spin coat method, a dip method, the roll coat method, the blade coat method, the doctor roll method, screen printing, etc. can be mentioned. A monolayer or multistory are sufficient as a recording layer. Generally the thickness (average thickness after desiccation) of a recording layer is in the range of 10-350nm, and the range of it is 30-250nm preferably. the case of the optical information record medium of this invention -- the thickness in the pre groove of a recording layer -- desirable -- the range of 50-200nm -- it is -- further -- desirable -- the range of 60-150nm -- it is the range of 65-120nm especially preferably. moreover, the thickness of a land -- desirable -- the range of 30-150nm -- it is -- further -- desirable -- the range of 40-120nm -- it is the range of 50-100nm especially preferably.

[0038] According to the above process, the optical information record medium of this invention which has a recording layer on a substrate can be manufactured.

[0039] The case where a reflecting layer and a protective layer are prepared is explained below. Generally a reflecting layer is prepared on a recording layer or a substrate for the purpose of improvement in the reflection factor at the time of informational playback. The light reflex nature matter which is the ingredient of a reflecting layer is matter with the high reflection factor to a laser beam. As the example Mg, Se, Y, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, A metal and semimetal, or stainless steel, such as

W, Mn, Re, Fe, Co, nickel, Ru, Rh, Pd, Ir, Pt, Cu, Ag, Au, Zn, Cd, aluminum, Ga, In, Si, germanium, Te, Pb, Po, Sn, and Bi, can be mentioned. Things desirable [among these] are Cr, nickel, Pt, Cu, Ag, Au, aluminum, and stainless steel. These matter may be used independently, or is two or more sorts of combination, or may be used as an alloy. It is the alloy which contains Au, Ag, and these metals preferably especially. A reflecting layer can form for example, the above-mentioned reflexivity matter on a recording layer or a substrate vacuum evaporations, sputtering, or by carrying out ion plating. the thickness of a reflecting layer -- general -- the range of 5-500nm -- it is -- desirable -- the range of 10-350nm -- it is the range of 30-200nm still more preferably.

[0040] A protective layer is prepared in order to protect a recording layer and a reflecting layer physically and chemically. as the ingredient used for a protective layer -- SiO, SiO₂, MgF₂, SnO₂, and Si₃N₄ etc. -- organic substances, such as mineral matter, thermoplastics, thermosetting resin, and UV hardenability resin, can be mentioned. As for a protective layer, being formed by resin is desirable.

When preparing a protective layer on a reflecting layer, a protective layer can be formed by laminating the film obtained with the extrusion of plastics on a reflecting layer through a glue line. Or a protective layer may be prepared by approaches, such as vacuum deposition, sputtering, and spreading. Moreover, in the case of thermoplastics and thermosetting resin, after dissolving these in a suitable solvent and preparing coating liquid, this coating liquid can be applied and a protective layer can be formed by drying. After dissolving in a solvent remaining as it is or suitable in the case of UV hardenability resin and preparing coating liquid, this coating liquid can be applied, and a protective layer can be formed by irradiating UV light and stiffening it. In these coating liquid, you may add [for the purpose of various additives, such as an antistatic agent, an antioxidant, and UV absorbent,] further. Generally the thickness of a protective layer is in the range of 0.05-70 micrometers.

[0041] The optical information record medium which has two recording layers can be manufactured by preparing two layered products which prepared the protective layer by the recording layer, the reflecting layer, and request on the substrate, and sticking with adhesives etc. so that each recording layer may serve as the inside. moreover, the obtained layered product, the substrate of this layered product, and abbreviation -- the optical information record medium which has a recording layer only in one side can be manufactured by sticking the same disc-like protective group plate of a dimension with adhesives etc. so that the recording layer may serve as the inside. UV hardenability resin which used adhesion for formation of said protective layer, and synthetic adhesives -- or it can carry out again using a double-sided tape etc. Thus, the adhesives layer formed is usually prepared by the thickness of the range of 0.05-70 micrometers (preferably 3-50 micrometers).

[0042] The informational record playback approach using the optical information record medium of this invention is enforced as follows, for example. Rotating an optical information record medium with a constant predetermined linear velocity (in CD format, it is 1.2-1.4m/second 1X) or a constant predetermined angular velocity, the laser beam for record of semiconductor laser light etc. is condensed through optical system from a substrate or protective layer side, and a recording layer is irradiated. Information is recorded by the exposure part of a recording layer absorbing the light, carrying out a temperature rise locally, and a physical or chemical change arising, and changing the optical property by the exposure of a laser beam. In this invention, the semi-conductor laser beam which has the oscillation wavelength of the blue glow of the semi-conductor laser beam which has the oscillation wavelength of the red light of the range of 620-690nm, and the range of 390-440nm, or purple-blue colored light as a record light is used. Moreover, as for record light, it is desirable that NA is condensed through the optical system of 0.55-0.7.

[0043] Playback of the information recorded as mentioned above irradiates the above-mentioned semiconductor laser light from a substrate or protective layer side, rotating the optical information record medium after record with a constant predetermined linear velocity, and is performed by detecting the reflected light. Even if a laser beam with the oscillation wavelength of which the above-mentioned range is used for the optical information record medium of this invention, record playback of it can be carried out. It is desirable to use the record playback approach reproduced using the semi-conductor laser beam which records in this invention using the semi-conductor laser beam which has the

oscillation wavelength of blue or a purple-blue color, and has red oscillation wavelength. There is an advantage reproducible using the record regeneration system already used widely as an object for DVD-R without using the regeneration system of the dedication which has the same oscillation wavelength as record light for the optical information record medium which recorded and manufactured image information by using this approach, using blue or a purple-blue color laser beam as for example, a record light.

[0044]

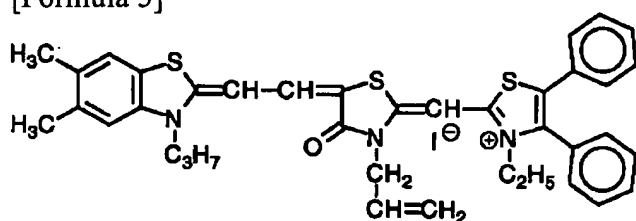
[Example] Below, the example and the example of a comparison of this invention are indicated.

[0045] [Example 1]

The disc-like resin substrate (0.6mm in the diameter of 120mm, the bore of 15mm, thickness) made from a polycarbonate (resin trade name: the panlight AD 5503 and Teijin, Ltd.) was produced using the injection molding machine which contains La Stampa produced so that it might become the production predetermined track pitch of a disc-like substrate, and a slot (pre groove). The track pitch of the concave slot (pre groove) of the obtained resin substrate The width of face of 90nm and a slot is 0.48 micrometers, and the depth of flute is whenever [190nm and tilt-angle / of the side attachment wall of a slot] (with extension of the straight line which connects the point on the side attachment wall of the slot in 10% of location of the depth of flute, and the point on the side attachment wall of the slot in 50% of location of the depth of flute from the base of a slot). The include angle formed in respect of being level on the base of a concave slot was 60 degrees. Measurement of these configurations was performed using AFM.

[0046]

[Formula 5]



[0047] It dissolved into 2, 2, 3, and 3-tetrafluoro-1-propanol, and the coating liquid for record stratification was prepared so that the concentration in the solution of the above-mentioned coloring matter might become 1 % of the weight. This coating liquid was applied to the front face in which that pre groove of the disc-like polycarbonate substrate obtained above is prepared with the spin coat method, it dried, the recording layer (thickness in a groove: 120nm, thickness:80nm of a land) was formed, and the optical information record medium (optical disk) according to this invention was manufactured.

[0048] [Evaluation as an optical information record medium]

(1) Using the following record regenerative apparatus, record power was changed to 3-10mW with a constant linear velocity of 3.5m/second, and the signal of a square wave with a frequency of 1MHz was recorded on the obtained optical disk by the optimal record power.

Record regenerative apparatus: DDU1000 (pulse tech company make)

laser: -- semiconductor laser pickup NA:0.6 rim intensity: with dispatch wavelength with a purple-blue color of 408nm -- the tangential direction 0.33 radial-direction deviation beam of 0.21 yen was used, and it carried out by a focus's using the knife-edge method and tracking using the push pull method. The refractive index n of the recording layer obtained to the laser beam with a wavelength of 408nm was 2.2, and the extinction coefficient k was 0.05.

[0049] The record signal was reproduced by 0.5mW laser power after record using the laser beam for record, and the laser beam of the same wavelength, and the modulation factor was measured. The modulation factor set to A the maximal value of the reflected light level of a direct-current playback wave when reproducing the signal recorded on the above-mentioned conditions, set the minimal value to B, set reflected light level when performing groove tracking at the non-Records Department to R, and

asked for it from the following formula.

Modulation factor (%) = $(A-B) / R \times 100\%$, consequently 62% of modulation factor was obtained.

[0050] (2) The semiconductor laser which has dispatch wavelength with a red of 638nm in the above-mentioned record regenerative apparatus was carried, and the signal was recorded on the optical disk like the above (1). The refractive index n of the recording layer obtained to the laser beam with a wavelength of 638nm was 2.3, and the extinction coefficient k was 0.1. Then, it reproduced using the laser beam of the same wavelength, and the modulation factor was measured by the same approach. Consequently, 65% of modulation factor was obtained.

[0051] (3) After recording a signal using semiconductor laser with dispatch wavelength with a purple-blue color of 408 above-mentionednm, when the signal recorded using semiconductor laser with dispatch wavelength with a red of 638nm was reproduced, the signal was reproducible in high resolution.

[0052]

[Effect of the Invention] By using the optical information record medium according to this invention, record playback is possible in the wavelength region of the laser beam of the laser beam for DVD-R and blue, or a purple-blue color. And the optical information record medium according to this invention shows good record reproducing characteristics in the laser beam of both wavelength regions. Therefore, the information recorded using the laser beam of blue or a purple-blue color is reproducible using the laser beam for DVD-R. Moreover, by using the laser beam of blue or a purple-blue color, it becomes more recordable [high density] and the optical, still bigger information record medium of storage capacity can be manufactured.

[Translation done.]